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AUTHORITY

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INHIBITED N_2O_4
Final Report

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Analytical Chemistry Group
Chemistry Section
Research Division

Rocketdyne
A Division of North American Aviation, Inc.
Canoga Park, California

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Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards Air Force Base, California
Air Force Systems Command
United States Air Force

FOREWORD

The research reported herein was supported by the Air Force
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sion, Edwards Air Force Base, Calif., Air Force Systems
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RPCL, serving as Project Monitor. This final technical
progress report was prepared under Rocketdyne G.O. 8728 in
compliance with Part I, Paragraph B, and line item 6 of
DD1423, and MIL-STD-847 (USAF).

The work described covers the period 1 July 1965 through
30 September 1966. The Responsible Scientist for this
program is Dr. Hubert E. Dubb of the Analytical Chemisty
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This report has been assigned the Rocketdyne report No. R-6781.

This technical report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
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ABSTRACT

This program is concerned with evaluating a new storable
liquid oxidizer INTO, which is nitrogen tetroxide (NTO)
inhibited with a fluorine oxidizer. The best fluorine
oxidizer has been found to be FNO_2.

Storability tests of INTO in stainless-steel, aluminum,
and nickel containers at 70 C have now been in progress
for 6 months with no apparent change in the composition
of the propellants.

Corrosion tests of steel and aluminum alloys are being
conducted in wet NTO, dry NTO, INTO made from wet NTO,
INTO made from dry NTO, and dry NTO + HF. The tests are
being conducted at ambient temperature for 30 days and
for 20 months, and at 70 C for 30 days. The results of
the 30-day tests are reported herein. A definite pass-
ivation layer was noted both visually and by weight change
on the aluminum samples exposed to INTO at both tempera-
tures and on the iron samples exposed to INTO and to NTO
+ HF at 70 C.

INTO made from wet and dry NTO has been intermittently
flowed through 25- and 100-pound valves for a 2 week period
with no apparent deterrent effects upon valve performance.

INTO has been prepared by bubbling F_2 through liquid-
propellant-grade NTO at ambient temperature. The reaction
proceeded smoothly and no difficulties are anticipated in
scaling up the operation.

The conductivities of INTO and NTO solutions have been
measured. The addition of FNO_2 or F_3NO to NTO caused only
a small change in conductivity. It is not anticipated
that INTO will present more galvanic corrosion problems
than does NTO.

Measurements of the vapor pressures and freezing points of
INTO solutions have been completed.

Methods have been developed for the chemical analysis of
INTO and of NTO.

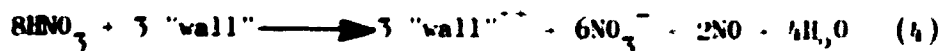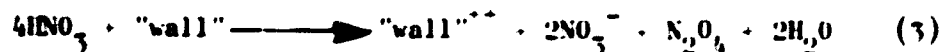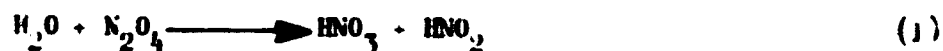# CONTENTS

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INTRODUCTION

Nitrogen tetroxide (NTO) is this country's most widely used liquid oxidizer. Corrosivity has greatly complicated the use of this propellant. Dry NTO is not a highly corrosive liquid, but moist NTO is extremely corrosive because of the formation of nitric and nitrous acids by the reaction of NTO with water. This moisture problem is the reason for the rigid and difficult-to-maintain military specification P-26539B (99.50-percent minimum N_2O_4, 0.10-percent maximum H_2O equivalent). Because up to 1 percent of water does not affect performance, the only reason for the highly restrictive 0.1-percent water equivalent requirement is to reduce corrosivity.

It has been assumed that nitrogen tetroxide presents no serious storage or handling problem when stored and transferred in clean, air-tight, moisture-free systems, and handled by trained personnel. This assumption has proved misleading for operational purposes.

The manifestation of corrosion effects has brought to light the moist NTO problem. In addition to causing material failures, the reactions of the moist oxidizer with the environment also lead to erosion phenomena. Because of the corrosion of container materials, a solid phase is often introduced into the system. The mechanical movement of this solid causes clogged filters, flow decay rates in metering equipment, intermittent irregularities, and unexpected residue appearance. Also, premature hardware failures, surreptitious leaks, and sporadic weakening of the auxiliary equipment have sometimes occurred because of a rapid, localized attack such as pitting and intergranular invasion of the nitrate species.

Briefly, NTO reacts with moisture to form HNO_3 and HNO_2. The HNO_2 then reacts further to form water and N_2O_3. The HNO_3 reacts with valve and container materials to form "salt" nitrate, water, and NO or N_2O_4. The NO then reacts with more NTO to reform HNO_3. The net result is a catalytic nitration of the materials of construction, with an increase in N_2O_3 but no decrease in the HNO_3 content of the NTO. That is, the solution,

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when nitrating the wall, loses none of its corrosivity as a result of the reintroduction of water into the system. The sequence of reactions can be summarized as follows:

$$H_2O + N_2O_4 \longrightarrow HNO_3 + HNO_2 \tag{1}$$

$$2HNO_2 \longrightarrow H_2O + N_2O_3 \tag{2}$$

$$4HNO_3 + \text{"wall"} \longrightarrow \text{"wall"}^{++} + 2NO_3^- + N_2O_4 + 2H_2O \tag{3}$$

$$8HNO_3 + 3\,\text{"wall"} \longrightarrow 3\,\text{"wall"}^{++} + 6NO_3^- + 2NO + 4H_2O \tag{4}$$

The care necessary to guarantee the integrity of a totally water-free system is often too rigorous to be practical.

Late in the summer of 1964, Rocketdyne developed the concept of INTO, which is NTO to which a fluorine oxidizer has been added. It was demonstrated by nuclear magnetic resonance (n.m.r.) and Turner bulb water equivalent analysis, that the NTO was purged of water by the reaction of fluorine oxidizers with the nitric acid present. One of the products of this reaction was definitely demonstrated to be HF. The technical position at that time was one in which it was known that (1) dry NTO is not highly corrosive, (2) wet NTO is highly corrosive, and (3) INTO consists of dried NTO with a fluorine oxidizer and HF present. IRFNA (RFNA with HF added) is less corrosive towards some alloys than is pure RFNA. By analogy, it was predicted that INTO should be less corrosive than wet NTO.

As a consequence of the experimental results summarized previously, the present program was initiated. The objectives of the program are (1) to choose a suitable fluorine oxidizer to make INTO, (2) to make an engineering evaluation of the corrosion properties and storability of the propellant, (3) to determine some of its basic physical and chemical properties, and (4) to develop methods for its complete chemical analysis.

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PHASE I: ENGINEERING EVALUATION

STORABILITY

Summary

One of the primary purposes of the INTO program has been to select the
most suitable fluorine oxidizer to add to NTO. Both F_3NO and FNO_2 seemed
likely candidates because: (1) either would react with HNO_3, (2) neither
should affect the propellant properties, and (3) both would allow a high
proportion of fluorine loading for a relatively small increase in vapor
pressure. As a result of the storability tests described below, F_3NO
was eliminated as a possible additive because it was found that it would
react with N_2O_4 to form FNO_2.

Experimental

NTO + F_3NO was tested for storability and constituents compatibility in
6061 aluminum, 1018 carbon steel, 321 stainless steel, and nickel con-
tainers at ambient temperatures, 53 and 70 C. The tests were carried out
under two conditions of bomb prepassivation: (1) mild, using F_3NO at 70 C
overnight, and (2) vigorous, using ClF_3 at 70 C overnight. The bombs had
a capacity of 8 to 10 milliliters and each was loaded with 4 to 6 grams
of a 4.9-percent F_3NO in NTO mixture.

The samples were analyzed by infrared spectrometry and gas chromatography
both immediately after loading and after appropriate time periods. The
data are summarized in Tables 1 through 3 .

An examination of the analytical data immediately reveals that the compo-
nents of the NTO-F_3NO mixture are not compatible at elevated temperatures.
As a result, emphasis on the program has been shifted exclusively to NTO
+FNO_2.

TABLE 1

STORABILITY OF NTO + F_3NO AT AMBIENT TEMPERATURE

Material	Mole Percent F_3NO at Start	Mole Percent F_3NO After 34 Hours	Mole Percent F_3NO After 80 Hours	Mole Percent F_3NO After 160 Hours
Stainless Steel (Working Solution Bomb)	4.9	--	--	4.6
321 Stainless Steel	4.9	3.4	3.3	2.3
Carbon Steel-1018	3.6	1.6	1.0	1.0
Al-6061	3.9	3.4	3.2	2.8
Nickel	4.2	3.4	3.5	3.2

Passivation: F_3NO at 1500 mm absolute pressure, STP, 24 hours at 70 C

Working Solution: 755 grams NTO plus nominal 5 mole percent F_3NO in 1-liter stainless-steel high-pressure bomb

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TABLE 2

STORABILITY AT 55 C

Material	Passivation	Mole Percent F_3NO at Start	Mole Percent FNO_2 at Start	Mole Percent F_3NO After 24 Hours	Mole Percent FNO_2 After 24 Hours	Mole Percent F_3NO After 80 Hours	Mole Percent FNO_2 After 80 Hours
321 Stainless Steel	1	4.0	0	0.4	2.9	0	0
Carbon Steel-1018	1	4.1	0	0.3	1.1	0	0
Al-606:	1	3.6	0	0.5	0	Trace	0
Nickel	1	3.8	0	0.3	3.3	0	4.0

Material	Passivation	Mole Percent F_3NO at Start	Mole Percent FNO_2 at Start	Mole Percent F_3NO After 24 Hours	Mole Percent FNO_2 After 24 Hours	Mole Percent F_3NO After 100 Hours	Mole Percent FNO_2 After 100 Hours	Mole Percent F_3NO After 30 Days	Mole Percent FNO_2 After 30 Days
321 Stainless Steel	2	2.3	0	0.8	4.0	0	4.2	0	4.3
Al-6061	2	2.7	0	0.7	2.9	0	4.7	0	4.8
Nickel	2	2.5	0	0.9	3.2	0	4.5	0	4.5

Material	Passivation	Mole Percent F_3NO at Start	Mole Percent FNO_2 at Start	Mole Percent F_3NO After 19 Hours	Mole Percent FNO_2 After 19 Hours	Mole Percent F_3NO After 44 Hours	Mole Percent FNO_2 After 44 Hours
Nickel Body with Monel Valve	3	3.4	0	1.5	3.8	0.25	4.1

Passivation:

1. F_3NO, 1500 mm Hg absolute pressure, STP, 24 hours, 70 C
2. Three of bombs used with passivation procedure 1 were further passivated with one atmosphere ClF_3 (STP) at 70 C for 24 hours
3. Single bomb previously used for reaction of 4 grams 50/50 F_3NO-NFO mixture at 70 C for 5 days

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TABLE 3

STORABILITY AT 70 C

Material	Passivation	Mole Percent F_3NO at Start	Mole Percent FNO_2 at Start	Mole Percent F_3NO After 34 Hours	Mole Percent FNO_2 After 34 Hours
321 Stainless Steel	1	4.0	0	0	0
Carbon Steel-1018	1	3.9	0	0	0
Al-6061	1	2.8	0	0	0
Nickel	1	4.1	0	0	2.5
					After 200 Days
321 Stainless Steel	2		4.3		4.2
Al-6061	2		4.8		3.9
Nickel	2		4.5		3.7

Passivation: 1 F_3NO, 1500 mm Hg absolute pressure, STP, 24 hours, 70 C

2 Three bombs previously passivated as in procedure 1, then further passivated with one atmosphere of ClF_3 (STP) at 70 C for 24 hours, and stored for 45 days at 53 C; temperature raised to 70 C and storage continued

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Because NTO + FNO_2 was formed by the reaction of F_3NO with NTO, the compatibility tests originally started with NTO +F_3NO were continued using the same solutions in the same bombs. The data from these tests are also contained in Table 1 through 3. These results indicate that NTO + FNO_2 is storable at elevated temperatures, in sufficiently passivated containers, for at least 6 months (45 days at 53 C and the remaining time at 70 C).

At the end of 6 months, the NTO + FNO_2 solution in the storability bombs had been completely used up by sampling for chemical analysis. The bombs were reloaded with a fresh NTO + FNO_2 solution and were returned to storage at 70 C. The storability tests are being continued and the contents of the bombs will be periodically analyzed.

CORROSION TESTS

Summary

The primary purpose of replacing NTO with INTO is to eliminate corrosion in field-use systems, or at least to reduce it to acceptable limits. Evaluation of improvements must be based on studies of the corrosive effects of INTO compared to the corrosive effects of NTO on the materials of construction used in propellant-handling systems. A limited series of screening tests were performed to evaluate the efficiency of the inhibitor.

An inspection of the materials in the Titan II engine system showed that an extremely large number of alloys and other materials are required for even this single application. It was far beyond the scope of this effort to evaluate the corrosion resistance of all of these materials to INTO. Instead, representative materials were selected for testing. These materials are presented in Table 4.

TABLE 4

MATERIALS SUBJECTED TO CORROSIVITY TESTING

Group I Iron Alloys	Group II Aluminum Alloys	Group III Nonmetals
304 Stainless Steel	6061-T6	Kel-F
316 Stainless Steel	7075-T73	Kynar
321 Stainless Steel	Tens 50	Butyl Rubber
AM350 SCT	2014-T6	Teflon
440C Stainless Steel	2024	Viton A
Welded specimens of all the above	Welded specimens of 6061, Tens 50 and 2014	

Because the investigation is basically comparative in nature, specimens were exposed to five different propellant compositions. These are:

1. Dry N_2O_4 (military specification, less than 0.10 weight percent H_2O equivalent and a minimum 99.5-percent assay)

2. Wet N_2O_4 (>0.1 weight percent H_2O equivalent)

3. Dry N_2O_4 plus approximately 3.0 weight percent FNO_2 ("dry INTO")

4. Wet N_2O_4 plus approximately 3.0 weight percent FNO_2 ("wet INTO")

5. Dry N_2O_4 plus approximately 0.5 weight percent HF

These compositions broadly cover the conditions that could be expected in actual operations. The fifth composition is included to check the effect of the major reaction product between the additive and water in the absence of either of these materials. Four series of tests were conducted: 30-days exposure at ambient temperature, 30-days exposure at 70 C, 20-months exposure at ambient temperature, and 7-days exposure at ambient temperature (nonmetals only).

At the start of the program, F_3NO was to be used as the inhibiting agent. As a result of the storability tests described supra, it was discovered that the F_3NO-NTO system was not stable and reacted to form FNO_2. It was subsequently shown that FNO_2 is as effective as F_3NO in reducing the water content of moist N_2O_4, and therefore FNO_2 was substituted for F_3NO as the inhibiting agent.

To date all 30-day tests have been completed, and all 20-month tests are in progress. The discussion and conclusions of this report are based only on data obtained from short-term (30-day) corrosion tests. At the end of the 20-month testing period, a supplementary report will be published.

Results of the 30-day tests have been promising. NTO with FNO_2 added forms a white passivation layer on aluminum alloys, both at ambient temperature and at 70 C. Control tests show that this layer is not caused by HF in solution. No passive layer is visible when ferrous alloys are exposed to FNO_2 but a green passive layer forms at 70 C because of HF in solution. Aluminum alloys are passivated by HF but only significantly so (visually apparent) at elevated temperatures. Aluminum is more heavily passivated by FNO_2 than by HF. In all cases, the FNO_2 passivation layers disappeared faster than the HF passivation layers when exposed to the atmosphere. The 304L, 316, and 321 stainless steel alloys and the 2014 and 2024 aluminum alloys appeared to be the most desirable of the alloys tested.

Procedures

Preparation of Specimens and Test Cylinders. The testing procedure was designed so that both welded and nonwelded specimens would be exposed to both the liquid and vapor phases of the propellant compositions. Materials were tested by exposing small disks (approximately 1/16-inch thick and 7/8-inch diameter) to the propellants. These disks were strung on rods and were separated by Teflon spacers. The spacers minimized interaction between individual specimens and ensured free penetration of the propellant to the surface of the specimens. Kel-F disks were placed between specimens to catch any residue that might have fallen off the surface of

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the specimens during testing. For material uniformity aluminum specimens
were strung on aluminum rods, ferrous specimens on stainless steel rods,
and nonmetallic specimens on Teflon rods. Tests were conducted in stain-
less steel and aluminum cylinders which were capped on one end and valved
on the other end (Fig. 1). Steel valves were used on the iron test bombs,
and aluminum valves were used on the aluminum test bombs.

Uniformity of specimens of each material was assured by cutting a suffic-
ient number of specimens to perform all tests from a single piece of stock.
Any heat treatment, cleaning, or other preparatory operations were per-
formed on the original stock before cutting the specimens. All specimens
were cleaned with a soap solution, rinsed with water and acetone and
weighed before testing. Each specimen was also stamped with a number and
a letter designating the test condition and alloy, respectively.

The test bombs, valves, and fittings were vapor degreased, washed with
soap and water, and rinsed with water, trichloroethylene, and acetone.
Valves were completely disassembled for cleaning and reassembled using
Fluorolube as a lubricant on the valve stem assemblies.

Preparation of Propellant Solutions. Individual solutions were prepared
by drying commercial NTO and then adding known amounts of the desired
additives. Water content was determined by nuclear magnetic resonance
(NMR) analysis and by aluminum Turner bulb analysis. HF and FNO_2 contents
were determined by infrared spectroscopy.

Loading. The propellant was loaded into the test bombs in a closed trans-
fer system (on a vacuum line). With reference to Fig. 2, a typical trans-
fer was carrier out as follows: The space between valve No. 1 and 2 was
evacuated, valve No. 2 was closed, and valve No. 1 was opened. With valves
No. 3, 4, and 5 open, the test bomb and loading assembly were evacuated.
Valve No. 4 was closed, and the loading assembly was pumped down to a
vacuum of approximately 10^{-3} torr. Valve No. 3 was closed and valve No. 4
was opened so that the test bomb was also pumped down to a high vacuum.
Valve No. 2 was opened and the loading assembly was allowed to fill for

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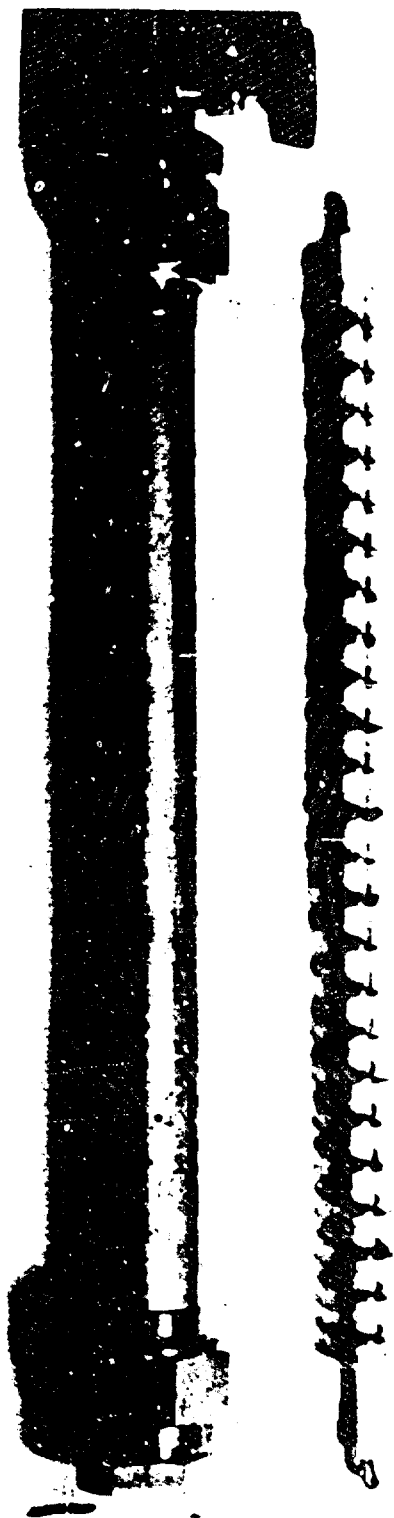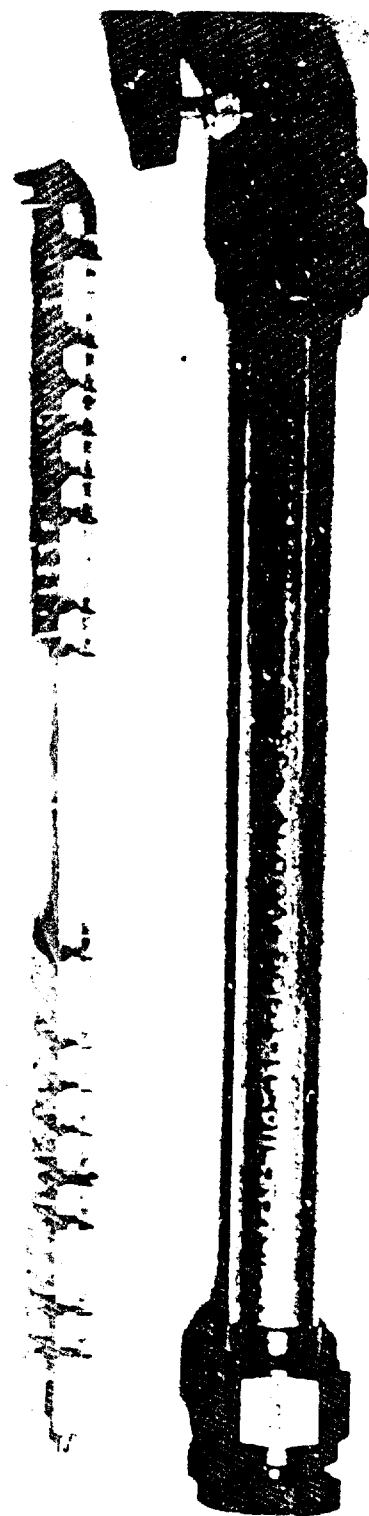
Fe Alloys   Al Alloys

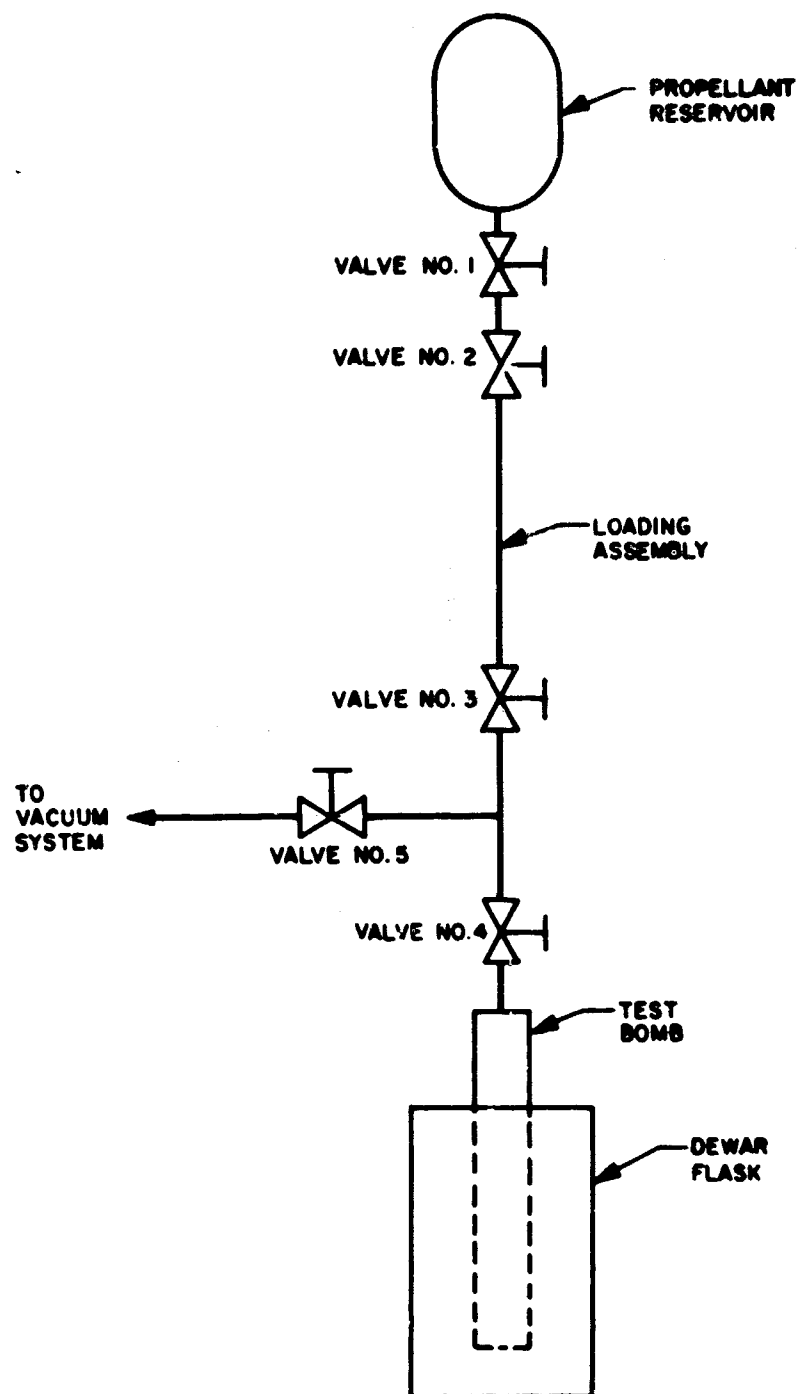Figure 1.   30-Day and 20-Month Test Specimens and Bombs

Figure 2. Loading Schematic

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5 minutes. After the loading assembly was filled, valves No. 2 and 5 were closed, isolating the loading system from the vacuum system and propellant reservoir. Valve No. 3 was then opened and the transfer was carried out for approximately 10 minutes. During the transfer, the Dewar flask was filled with liquid nitrogen to bring the test bomb temperature down to -196 C. Upon completion of the transfer, valves No. 3 and 4 were closed and the bomb was removed from the loading system. The bomb was then weighed to verify transfer of a 65 milliliter volume. Smaller bombs and a smaller loading assembly were used for the nonmetal samples.

Testing. All bombs were stored in an inverted (valve down) position. The ambient and high-temperature bombs were stored in an outdoor bay at the Rocketdyne Canoga Park facility. The high-temperature bombs were stored in an oven at 70 ± 3 C. Periodic samples were taken of the liquid contents of all bombs containing HF or FNO_2 on a vacuum line, to which a gas sampling cell was attached, as follows: The test bomb was attached to the line in an inverted position. The sampling system was evacuated and then passivated with pure FNO_2. After evacuating the FNO_2 from the system, the valve on the test bomb was barely opened expanding a liquid sample to the gas phase in the sampling system. At the desired pressure, (200 mm of Hg) the test bomb valve was closed and the infrared or near infrared sample cell was shut off and removed from the system and analyzed as described in the Phase II section of this report.

Evaluation of Tests. All corrosion tests were evaluated in the same manner to ensure a common basis of comparison. An overall observation of the specimens, including the taking of color photographs, was made immediately upon removal from the test bombs. The alloys which had been obviously affected by exposure to the oxidizer were noted. For the nonmetallic samples, visual observations were made for swelling, dissolution, and cracking. Weights of each specimen were then taken to determine the absolute and percent weight change. The metallic specimens were then photomicrographed at 15X magnification. Observations on the surface condition of the specimens were made by a comparison of the photomicrograph of the

exposed specimen to a photomicrograph of a control specimen. Photomicrographs of two ferrous and two aluminum alloys with controls are presented in Fig. A-1 through A-12 of Appendix A.

For the nonmetallic specimens, NTO continued to evaporate long after removal from the test bomb, therefore weights were taken after 72 hours and 240 hours.

Unloading of Test Bombs. Unloading procedures were designed to preserve the condition of the specimens as they were upon removal from the test bombs. The nonmetallic samples were removed and analyzed in the atmosphere. After dumping the liquid from the bomb, the samples were removed from the bomb, removed from the Teflon r , and allowed to dry on a tray. Observations were made on the samples, and they were then weighed after 72 and 240 hours.

The initial unloading procedure for the metallic specimen tests was used for the ambient temperature, wet, and dry NTO tests. After dumping the liquid from the test bombs, the specimen strings were rapidly placed in a glove bag (portable plastic bag with attached gloves) through which a dry gaseous nitrogen purge was run. When the strings of coupons no longer showed signs of degassing NTO, they were removed from the glove bag and given three rinses: methanol, 50-percent methanol/50-percent water, and water. The purpose of the rinses was to remove any residual nitric acid which would continue to corrode the specimens. The specimens were then removed from the rods, blotted dry, photographed, and weighed.

The procedure was modified for the removal of the aluminum specimens from the ambient temperature, dry INTO test bomb. Modifications were made to preserve the passivation layer. After dumping the liquid, a dry gaseous nitrogen purge was run through the bomb. The bomb with the specimen string inside was placed in the glove bag where the specimens were then removed from the rod. The specimens had a thin white passivation layer. One specimen was removed and weighed. It appeared to be losing weight.

After approximately 1.5-hours exposure to the atmosphere, the layer disappeared. After 24 hours in the glove bag, the remaining samples showed significant passivation layer loss. It was apparent that a more inert atmosphere than that available in the glove bag was required for preserving the passivation layers.

All tests subsequent to the aluminum alloys in dry INTO were opened in a dry box purged by a moisture-free gaseous nitrogen. The dry box is approximately 4 by 3 by 3 feet with an antechamber which enables hardware to be placed into and removed from the box while maintaining an inert atmosphere. A Mettler balance was placed in the box enabling the weighings to be made in an inert atmosphere. The only work conducted in the atmosphere was the dumping of the liquid, the gaseous nitrogen purging of the INTO test bombs, the rinsing of the NTO test samples, and the photographing of the specimens. All weighing and removal of the samples from the rods was conducted in the dry box. An attempt was made to preserve the passivation layers by sealing the specimens in Saran Wrap packets upon removal from the dry box. This preservation technique was sucessful in some cases and inadequate in others. This unloading procedure proved satisfactory for all tests.

Test Results

Nonmetal Tests. Seven-day nonmetals compatibility tests based on weight change and visual observations were carried out in NTO, NTO + F_3NO, and NTO + FNO_2. These tests were conducted identically to the metals tests except for the preparation of the NTO + FNO_2 test bomb. The stainless steel bomb used in the NTO + FNO_2 test was prepassivated with an NTO + FNO_2 solution containing 3.0 mole percent FNO_2. The solution remained in the bomb for 24 hours at 23 C.

The liquid and vapor phase specimens appeared to be identically affected during both the NTO + F_3NO and NTO tests (Fig. A-13). Kel-F, Kynar, and Teflon appeared unaffected except for color changes. The Viton A cracked

in both NTO and NTO + F_3NO. Butyl rubber was completely dissolved in NTO + F_3NO and seemingly unaffected by NTO. The F_3NO in the NTO was not completely destroyed by the reaction with the butyl rubber.

The results of the NTO + FNO_2 test were markedly different from those of the NTO + F_3NO test (Fig. A-14). Kel-F, Teflon and Kynar again appeared unaffected by either NTO or NTO + FNO_2 except for color change and a very slight surface softening. The Viton A exposed to both NTO and NTO + FNO_2 exhibited extreme swelling (nearly twice the original size) as observed upon removal from the test bombs. After exposure to the atmosphere for 30 minutes, the specimens reduced in size to approximately one and one-tenth the original size. There was some splitting around the inside diameter of the specimens exposed to the liquid phase of both the NTO and the NTO + FNO_2. The Viton A exposed to liquid phase NTO + FNO_2 had approximately one-fourth the resiliency of the control specimen compared to approximately three fourths for the specimen exposed to the liquid phase NTO. In addition, the Viton A specimen exposed to liquid phase NTO + FNO_2 was the only specimen which lost weight.

Although the butyl rubber also exhibited extreme swelling as observed immediately upon removal from the bomb, the swelling was not as great as that of the Viton A, and there was no cracking. After exposure to the atmosphere for 30 minutes, the specimens returned to their original size. The weight changes of the specimens, along with observations, are presented in Tables A-1 and A-2.

In summation, there was considerably less reaction between the nonmetals and NTO + FNO_2 than between the nonmetals and NTO + F_3NO. There was little reaction between NTO + FNO_2 and the butyl rubber, whereas the NTO + F_3NO dissolved nearly all of the butyl rubber. The amount of remaining inhibitor was also greater in the NTO + FNO_2 test. Pretest FNO_2 content was 3.0 mole percent (in the supply bomb) and posttest FNO_2 content was 1.5 mole percent (in the test bomb).

Wet and Dry NTO Tests. The ferrous and aluminum specimens exposed to wet and dry NTO appeared, in general, only very slightly corroded if affected at all. The only two alloys which were consistently affected by exposure were 1018 carbon steel and 440C stainless steel. Both were slightly discolored upon removal from the ambient test bombs. The 440 showed obvious flaking in the dry NTO high-temperature test and discoloration in the wet NTO high-temperature test. The welded carbon steel specimens appeared black in the wet NTO high-temperature test. A sticky surface residue was apparent on the vapor phase carbon steel specimens in the dry NTO high-temperature test. Except for some spotting of the wet NTO high-temperature test specimens, none of the aluminum alloys appeared affected.

A yellow-green powder was observed on the aluminum and ferrous alloys in the ambient tests. Samples of this powder were taken and analyzed by emission spectrographic analysis. Results of these analyses are presented in Table 5 . Because iron is a major constituent even in the residue from the aluminum test sample, it is believed that the source of the iron is not from the test bombs but from the container used for storing the NTO before loading. Several of the other elements are stainless steel constituents. These could come from the test bombs or, more likely (because they also are present in the aluminum test sample), from the storage container.

TABLE 5

EMISSION SPECTROGRAPHIC ANALYSES OF NTO TEST RESIDUES

Test	Major Constituents	Minor Constituents	Minor-Trace Constituents	Trace Constituents
Dry NTO, 30-Day Ambient, Ferrous Alloys	Fe	--	Cr, Al, Si, Mg, Ni, Mo, Cu, Ti, Na	Zr
Wet NTO, 30-Day Ambient, Ferrous Alloys	Fe, Cr	Ni, Cu	--	Mn, Ti, Mg, Zr, Al, Si
Wet NTO, 30-Day Ambient, Aluminum Alloys	Fe	Cr, Ni, Cu	Si	Mn, Mg, Zr, Al

Each specimen was weighed before and after testing. The weight changes presented in Tables A-3 through A-13 are averages based on four samples of each alloy (one welded and one nonwelded in each the vapor and liquid phases). The only exceptions to this averaging of four samples are for the 2024 and 7075 aluminum alloys (one nonwelded sample in each phase) or where otherwise noted in the comments.

For the ambient temperature tests (Tables A-3 and A-4), most of the weight changes are not really significant relative to the probable errors incurred during handling and reweighing the specimens after the tests.

The weight changes are valid to approximately ±0.0002 grams. This represents approximately ±0.0009 and ±0.023 weight percent for the ferrous and the aluminum alloys, respectively. Of the 22 averages in Tables A-3 and A-4, 17 are within this range. There are 8 weight increases and 11 weight decreases which again show a random scatter in the data.

Weight changes are more significant for the high-temperature tests (Tables A-5 and A-6. The 300-series ferrous alloys in the dry NTO test again showed insignificant changes. The conditions apparently were still not severe enough to affect these corrosion resistant alloys. The 440 and 1018 alloys showed weight gains which are consistent with visual observations (flaky, discolored surface layers). The ferrous alloys in the wet NTO test showed significant weight losses in all cases. The conditions were severe enough to bring about a corrosive effect. Except for the 2014 in the dry NTO test, all aluminum specimens in high-temperature NTO tests exhibited weight losses. Although not all of these weight changes were of significant magnitude, the direction of the weight changes (losses) implied a corrosive process in action.

Comments on the surface condition of the specimens made from the comparison of photomicrographs of control and exposed specimens are presented in Tables A-14 through A-22. Samples of these photomicrographs are shown in Fig. A-1 through A-12. Because the interpretation of the photomicrographs is inherently subjective in nature, observations were made by two people independently, and the comments made are a compilation of these

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observations. Although observations were made on photomicrographs of two specimens in each phase (except for 2024 and 7075 aluminum), in Tables A-14 through A-22, the observations have been presented as vapor and liquid phase comments. In almost all cases, the welded and nonwelded samples exhibited the same effect in a given phase. Most of the comments in Tables A-14 through A-17 express minimal surface **attack** or no effect at all. These comments substantiate the minor or insignificant corrosion reflected by the NTO tests discussed above.

In conclusion, the results of the NTO corrosion tests are as follows. The conditions in the ambient temperature test were not severe enough to show corrosive action. Although no large weight losses were evident (none greater than 1 percent), the weight losses for the aluminum specimen in the high-temperature tests and the ferrous specimens in the high-temperature wet NTO test showed a corrosive process in action. It is anticipated that the 20-month ambient tests will yield data which will confirm **the** corrosive trend apparent in the high-temperature tests.

Dry INTO Tests. The results of the dry INTO (NTO $-$ FNO$_2$) tests with aluminum are most promising in that an obvious white passivation layer was formed on all specimens for both ambient and high-temperature tests (Fig. A-15 through A-18). The ferrous specimens showed no visible layers. The only visible effect with the ferrous specimens was a discoloring of 1018 carbon steel and 440C stainless steel alloys in both the ambient and high-temperature tests. The ambient, aluminum alloy test was run twice. The first time the test was run, infrared analysis showed that there was no FNO$_2$ present in the bomb when it was opened, and the passivation layers reacted while in the glove bag, yielding no photomicrographs and questionable weight changes. When the test was rerun, the unloading was conducted in a dry box as discussed above.

The aluminum alloys showed **weight** increases ranging from 0.7 to 3.6 weight percent (Tables A-7 through A-9). The layers on 6061 and Tens 50 appeared very loose relative to the other alloys. The layers on 2014 and 2024 appeared much thinner and more adherent than those on 6061 and Tens 50.

The integrity of the 7075 layers fell between that of the 6061-Tens 50 and the 2014-2024 layers. Photomicrographs were taken of the aluminum specimens from the ambient temperature test which was rerun. The layers on the specimens from the initial ambient test and the high-temperature test reacted before photomicrographs could be taken. The comments on the surface condition for the ambient test specimens (Table A-18) support the observation that the layers on 2014 and 2024 were thinner (and probably more adherent) than those on the other alloys.

The ferrous alloys showed weight changes ranging from 0 to plus 1.2 percent (Tables A-7 and A-9). The 304, 316, and 321 alloys showed less of a weight gain than the other alloys in both the ambient and high temperature tests. For 304, 316, and 321, the weight gains were greater in the ambient temperature test than the high-temperature test. For AM 350, 440, and 1018, the trend was reversed. Observations of the photomicrographs (Tables A-18 and A-19) showed that these weight increases were caused by thin surface layers. These layers can be attributed to either the FNO_2 in solution or the HF in solution formed from the reaction of FNO_2 with the water in the NTO (dry NTO is not completely water-free).

All test bombs with dry INTO exhibited a decrease in FNO_2 concentration with time. The decrease was caused by passivation of the test bomb and samples. It is anticipated that during the 20-month tests, the FNO_2 concentration will be constant after complete passivation of the bomb and samples has occurred. This passivation phenomenon is consistent with the results obtained in the storability tests discussed in a previous section of this report.

Wet INTO Tests. The aluminum specimens in wet INTO also formed white passivation layers (Fig. A-19 and A-20). The layers on the high-temperature test specimens were much heavier than those of the ambient temperature test. Especially in the case of the high-temperature specimens, the layers on 2014 and 2024 appeared much more adherent than those on 6061, Tens 50, and 7075. The ambient-temperature ferrous specimens showed no white layers. The high-temperature ferrous specimens exhibited light green passivation layers in the case of the 300-series alloys and grey layers in the case

of the 440 and 1018 alloys (Fig. A-21). The layers on 304, 316, and 321 were very thin compared to the layers on AM 350. Because the high-temperature, dry INTO, ferrous specimens did not passivate and the high-temperature, wet INTO specimens did, it appears that the passivation layer on the ferrous alloys is not primarily due to FNO_2 but to a reaction product of FNO_2 and water, HF. Furthermore, because the ambient-temperature specimens did not passivate as did the high-temperature specimens, HF passivation on the ferrous alloys is significant only at high temperature in a 30-day test.

The ambient aluminum alloys showed weight increases of 0.8 to 4.6 weight percent (Table A-10). The high-temperature alloys showed increases of 5.4 to 23.2 weight percent (Table A-11). As can be seen from the range of weight changes, the high-temperature specimens did passivate much more heavily than the ambient specimens. Photomicrographs were taken for the ambient aluminum specimens but not for the high-temperature specimens (layers reacted before pictures could be taken). Comments on these photographs (Table A-20) substantiate the observed layers.

The ferrous alloys showed weight increases of 0.02 to 0.15 weight percent for the ambient-temperature alloys and 0.35 to 1.71 for the high-temperature alloys (Tables A-10 and A-11). The 304, 316, and 321 specimens showed less weight gain than the other alloys in both tests. The larger weight gains for the high-temperature test reflect the observed passivation layers. The weight increases of the ambient test specimens are significant and reflect thin surface layers. These layers were observed on the photomicrographs as the comments on the pictures confirm (Tables A-19 and A-20).

The decrease with time of FNO_2 concentration was faster in the wet INTO bombs than in the dry INTO bombs. FNO_2 had to be replenished in 3 of the 4 tests before the 30-day test period was completed. The reasons for this rapid dissipation of FNO_2 is that FNO_2 not only must passivate the bomb and specimens, but it must also react with the water present. Passivation is essentially the only reaction in the dry INTO.

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Dry NTO + HF Tests. The high-temperature tests exhibited thin passivation layers, whereas the ambient temperature test specimens were not significantly affected. The aluminum specimens exhibited very thin, white layers (Fig. A-22). The ferrous specimens showed very thin, light green, passivation layers (except for 440) especially in the vapor phase (Fig. A-23). The 440 specimens exhibited heavy, cracked and peeling, dark colored layers. The layers on 1018 and AM 350 were heavier than those on 304, 316, and 321. The only three alloys of the ambient tests which exhibited obvious surface changes are Tens 50 aluminum, 1018 carbon steel, and 440 stainless steel. It is significant that the layers formed on the aluminum specimens are much thinner than those formed on the aluminum specimens exposed to wet and dry NTO. It is also noteworthy that aluminum did not show a passivation layer in the ambient temperature test. In a 30-day test, it appears that HF will significantly passivate aluminum and ferrous alloys only at elevated temperature.

The ambient-temperature aluminum alloys showed weight increases of 0.04 to 0.12 percent (Table A-12). The high-temperature aluminum alloys showed increases of 1.67 to 3.59 weight percent (Table A-13), a marked increase over the ambient changes due to the greater passivation. It is noteworthy that in the high-temperature test, 2014 and 2024 showed the smallest percent weight gains. This implies thinner (and perhaps more adherent) layers than those on the other alloys as was the case in the NTO solutions. Comments on the surface condition (Tables A-21 and A-22) verify the much lesser affect of the solution on the 2014 and 2024 alloys. It should be noted that the reported weight gains reflect the slight layers observed on the ambient aluminum specimens (Table A-21).

The ambient ferrous alloys showed weight gains of 0.03 to 0.22 percent (Table A-12). The high-temperature alloys exhibited 0.16 to 1.98 percent weight gains (Table A-13). Again, the heavier weights for the high-temperature test reflect the heavier passivation layer. The 304, 316, and 321 alloys showed the smallest weight gains in both tests as was the case in the NTO solutions. The comments on surface conditions (Tables A-21 and A-22) are in accordance with the visual observations and weight changes.

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Conclusions and Recommendations

The conclusions made below are based on 30-day ambient and high-temperature (70 C) tests. It is assumed that the results of the 20-month tests will not conflict with the data already obtained. The significant results are as follows:

1. Wet NTO will corrode aluminum and ferrous alloys at elevated temperature.

2. FNO_2 will passivate aluminum alloys at ambient and at elevated temperature.

3. HF will passivate both aluminum and ferrous alloys but only significantly (visually apparent) at elevated temperatures.

4. FNO_2 does not significantly passivate ferrous alloys.

5. Passivation layers on aluminum are much heavier with FNO_2 than with HF

It was apparent that certain aluminum alloys and certain ferrous alloys withstand far better than the 1018 carbon steel, 440C stainless steel, and the AM350 SCT alloys. Wherever corrosion was evident, the 300-series stainless steels showed smaller weight losses, hence, less attack than the other alloys. Wherever passivation was evident, the 300-series stainless steels showed, in general, smaller weight gains (thinner and probably more adherent layers) than the other alloys. The 1018 carbon steel and 440C stainless steel exhibited highly undesirable surface conditions in certain cases; e.g., high-temperature, dry NTO + HF test.

Considering the aluminum alloys, the 2014 and 2024 alloys appeared to be more desirable than the other whenever passivation was evident. The layers on 2014 and 2024 appeared much thinner and much more adherent than those on the other alloys. The layers on 6061 and Tens 50 often exhibited a powdery or flaky texture which would be undesirable for use in a system. Although the layers on 7075 aluminum were not quite as loose as those on 6061 and Tens 50, the alloy did not appear to be as desirable as either 2014 or 2024.

This study is comparative and, hence, subjective in nature. The comments made above are based on overall impressions and averages. Individual specimens could be found which would contradict the conclusions drawn. It should also be noted that the alloys which appeared most desirable are only the most desirable of the ones tested. To judge which alloys would work best with INTO, a much larger number of alloys would have to be tested. Before any INTO system is made operational, the particular alloys to be used must be tested in a study similar to the one conducted.

GALVANIC CORROSION

Summary

System compatibility is dependent on factors beyond the simple corrosive effects of the propellant on the individual materials of construction. One of the most important interactions is galvanic corrosion between dissimilar metals exposed to the propellant. While there is no exact correlation between conductivity and galvanic corrosion, the data obtained here will help determine the necessity of later direct studies, because more conductive solutions have a larger tendency to exhibit this type of corrosion phenomenon.

Experimental

The electrical conductivity of the following seven propellant mixtures have been measured.

Composition	Conductivity x 10^{12} ohm^{-1} cm^{-1}
Dry NTO (<0.01 weight percent H_2O)	7
Dry NTO + F_3NO (2.0 weight percent)	15
Dry NTO + HF (0.3 weight percent)	3
Wet NTO (>0.1 weight percent H_2O)	9
Wet NTO + F_3NO (2.0 weight percent)	4
Dry NTO + FNO_2 (5 weight percent)	40
Wet NTO + FNO_2 (5 weight percent)	34

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The electrical conductivities were measured by a technique used previously
for chlorine pentafluoride (Ref. 1). A Kel-F conductivity cell, equipped
with nickel electrodes was used. An impedance bridge, which measures a
simple equivalent circuit (a resistor and a capacitor in series), was used
to measure the series impedance and the a-c resistance at 1 kilocycle of
the cell containing the propellant. From such measurements and the physical
dimensions of the cell, the conductivities of the fluids were calculated.

The conductivity cell was preconditioned by soaking with propellant grade
NTO. A Fluke Model 710B Impedance Bridge (accuracy ±0.1 percent) was used
to make the a-c (1000 cycles) resistance measurements. To improve bridge
sensitivity, cell capacitance was balanced by the addition of external
capacitors. The maximum resistance which can be measured directly by the
bridge is 11 megohms. Because the resistance of the cell exceeded this
value for all three measurements, the cell resistance was found by measur-
ing the decrease in resistance of a 9.56 megohm (a-c resistance) restrictor
when shunted by the cell. This method becomes less precise at very high
cell resistances.

For example, for a cell resistance of 1000 megohms, the precision is ±10
percent. With measurements of exceedingly low conductivities, it is very
difficult to achieve reproducibility to better than an order of magnitude.
Addison, et al. measurements on NTO (Ref. 2), which were carried out with
d-c rather than a-c circuitry, were fairly precise electrically, but the
reproducibility from sample to sample was not precise. Conductivities
varied from 1×10^{-12} to 8×10^{-12} ohm^{-1} cm^{-1}. Their method of NTO pre-
paration, the thermal decomposition of $Pb(NO_3)_2$ followed by drying over
P_2O_5, should have been capable of yielding very high quality NTO.

It was considered unnecesary to equip the conductivity cell with a thermo-
stat because the temperature coefficient of conductivity of NTO was not
great enough to significantly affect the measurements. For example,
experimental conductivities found by Addison were 1.71×10^{-12} ohm^{-1} cm^{-1}
at 13.6 C and 2.24×10^{-12} at 20.4 C.

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A cell constant of 0.0096 cm^{-1} was calculated by measuring the conductivity of a 0.010 N KCl solution and using a value for its specific conductivity of 0.00136 ohm^{-1} cm^{-1} (Ref. 3).

Conclusions

Because of the low conductivities measured for the INTO solutions, it is not anticipated that galvanic corrosion will be more of a problem with INTO than it is with NTO.

CORROSIVE EFFECTS OF FLOWING INTO

Summary

The study to determine the corrosive effects of static and flowing inhibited nitrogen tetroxide on typical Rocketdyne Small Engines Division(SED)pro- pellant valves has been completed. The SED propellant valves used for the study were Gemini-type capsule 2 and 3 design. The test sequence was a combination of dynamic and static conditions.

The valves were exposed to the inhibited nitrogen tetroxide for a 14-day test period at ambient temperatures, and during the test period the valves were cycled daily. The daily cycle served first as a check to see if the valves were operational, and to allow fresh propellant from the reservoir to flow into and through the valves. Pre- and post-valve functional test were performed. A posttest disassembly and inspection of the valves was conducted, as well as pre- and post-analysis of the propellant. Wet and dry nitrogen tetroxide with the inhibitor (FNO_2) were tested.

Test Procedure

Four propellant valves, Gemini-type capsule 2 and 3 design, were selected as being typical of SED hardware. These were two 25-pound thrust and two 100-pound thrust valves (Fig. B-1 through B-4). These particular valves

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were previously research and development valves that were assembled for a controlled decontamination study, but were never used.

The selected valves contained typical fabrication materials, close-tolerance clearances, and had proved their design in prior compatibility testing with Military Specification nitrogen tetroxide. Prior to testing, the selected propellant valves were precision cleaned (Rocketdyne level 4) and were functionally tested, reflushed with freon TF, and packaged for testing.

The experimental setup for the compatibility test was constructed of stainless steel as shown in Fig. B-5 and B-6. Each component of the system (tank lines, hand valves, etc.) was precision cleaned in the same manner as the valves. After assembly of the experimental setup, and prior to installation of the propellant valves, the system was flushed with freon TF to ensure that the system had not been contaminated during assembly. When the cleanliness of the system had been reassured, the propellant valves were installed and tested as follows.

Two of the four valves (i.e., one 25-pound thrust valve and one 100-pound thrust valve, identified as No. 1 and 2) were exposed to Military Specification NTO with inhibitor added. The remaining two valves (one 25-pound thrust valve and one 100-pound thrust valve) identified as No. 3 and 4 were exposed to NTO with water equivalent in excess of Military Specification plus the inhibitor.

The propellant reservoir tanks were removed from the system and loaded with propellant. After the tanks were filled, they were assembled into the test system. The pretest and posttest analysis of the propellant is shown in Table B-1.

During the 14-day test period, the valves were actuated once a day. Propellant was observed being expelled during each actuation, ensuring that the valves were operational. Observation of the propellant was made by watching the vent port of the propellant catch tank as shown in Fig. B-5. Valve actuation was done with a power supply capable of delivering 26 vdc.

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Throughout the 14-day test period, no additional propellant was required other than that stored in the test system reservoirs.

Upon completion of the prescribed test period, the subject valves were removed from the experimental setup, decontaminated, and packaged for further testing. Decontamination of the propellant valves was accomplished only with gaseous nitrogen purges so as not to **disturb** or remove any film or reaction products prior to posttest functional testing and subsequent disassembly.

Test Results

All four propellant valves successfully completed the prescribed test conditions. The pre- and post-functional data show that there was not deterioration of the valves caused by the inhibitor (FNO_2) added to the nitrogen tetroxide (Table B-2). Examination of the hardware with the unaided eye and at 10, 15, and 45 diameters, showed a coating on all the metal surfaces of a white to pale green color, most probably iron fluoide (Table B-3). There was no deterioration of the base material of the propellant valves.

Conclusions

1. All four Gemini-type propellant valves were operational at the end of the 14-day dynamic/static exposure to inhibited nitrogen tetroxide.

2. Pre- and post-functional tests of the four Gemini-type propellant valve showed no significant changes (Table B-2).

3. No deterioration of the materials of construction was observed (Fig. B-3 and B-4).

4. A nearly uniform white to pale green coating was observed on all internal surfaces of the propellant valves at the conclusion of the tests.

5. Inhibited nitrogen tetroxide is compatible with the SED solenoid valves tested on this program.

TRANSFER EFFECTS

Summary

If INTO is to be developed into a field operational propellant, it will be necessary to make the INTO, transfer it into a shipping container, then to a storage tank, and finally into a motor while still maintaining its integrity. Determining the effects of transferring INTO was thus of prime importance.

Experimental

INTO has been transfered from a 1-liter 304 stainless steel Hoke cylinder into corrosion test bombs and storability bombs over 25 times. Analysis was performed of samples of the liquid phase of the INTO in the Hoke cylinder and in the bombs loaded from the cylinder. When the bombs being loaded were prepassivated, no significant change in FNO_2 content was noted. When the bombs were not prepassivated, the FNO_2 content dropped until passivation occurred. There was also some drop in FNO_2 content of the liquid INTO when there was a significant ullage remaining in the bombs after loading, because the FNO_2 is enriched in the ullage.

Conclusions

It is possible to transfer INTO without significantly decreasing its FNO_2 content. From a practical consideration, it would be best to prepassivate containers into which INTO is to be loaded and to attempt to leave as little ullage as possible. Prepassivation could best be accomplished by loading with a small quantity of INTO and then venting this small portion.

RECLAMATION

Ten samples of out-of-specification NTO have been reclaimed by the addition
of fluorine oxidizers. F_3NO has been used to reclaim NTO containing as
much as 0.22 weight percent H_2O. FNO_2 has been used to reclaim NTO con-
taining as much as 0.24 weight percent H_2O. FNO_2 formed in situ by the
addition of fluorine has been used to reclaim NTO containing as much as
0.19 weight percent H_2O. The original water contents were determined by
nuclear magnetic resonance and Turner bulb techniques, and the final
water contents were determined with glass and aluminum Turner bulb apparati.
The final water contents were in the range of 0.02 to 0.04 weight percent.
It is probable that the final values obtained are not zero only because of
reaction of HF or FNO_2 with the apparati.

FIELD PREPARATION OF INTO

Summary

One of the most promising aspects of using FNO_2 as an additive in NTO has
been the possibility of forming FNO_2 in the field by the reaction of F_2
with NTO. This possibility has been investigated on a bench scale with
complete success. No major difficulties are anticipated in further scal-
ing up the operation.

EXPERIMENTAL

A 1-liter passivated Hoke cylinder was loaded with 1120 grams (750 C) of
liquid N_2O_4. Provisions were made for the withdrawl of liquid samples and
of samples of the gas above the liquid as well as measurements of pressure
(Matheson SS gage 23538-1) and temperature (Tem-Tron thermocouple U-T2)
changes (Fig. 3). The gaseous fluorine was stored in a 500-cc Hoke
cylinder reservoir at 50 to 60 psig and was bubbled through the liquid
N_2O_4 in small increments by means of the pressure differential. The de-
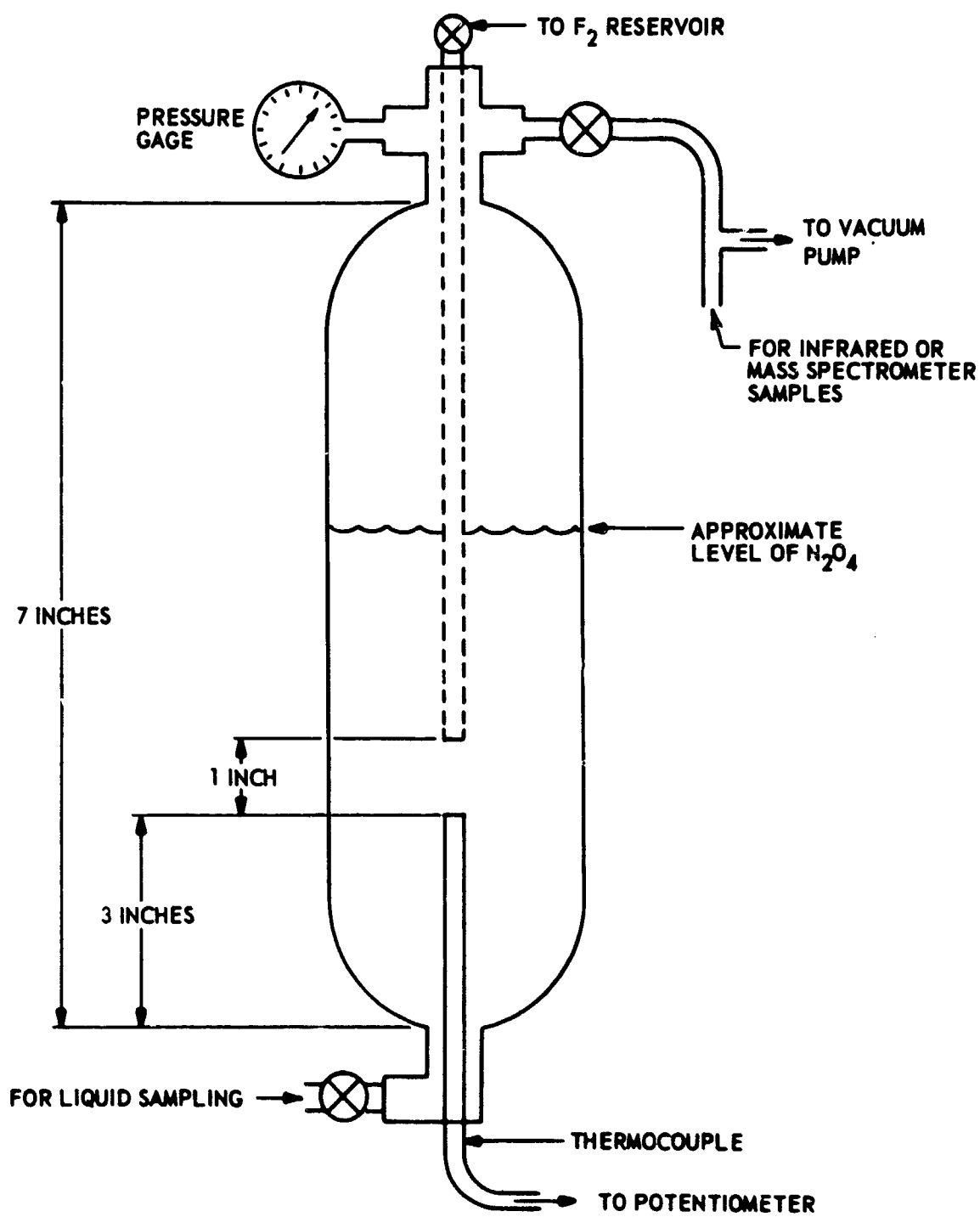tails of the addition are summarized in Table 6.

Figure 3. Field Preparation of INTO

TABLE 6

SUMMARY OF FLUORINE ADDITION DATA

Step Number	Number of Increments	Amount Added, cc	Time, hours	Gas-Phase Pressure, psig	Liquid Temperature Changes	Gas phase Products of N_2O_4
I	18	1200	5	20	None	None
II	11	1250	22	45	None	None
III	6	1100	1	45	None	FNO_2
IV	9	1800	24	56	None	FNO_2
V	*	1250	—	—	None; warm in gas-phase area	FNO_2
VI	*	650	—	—	None	
VII	1	750	—	—	None	
VIII	**	2100	—	—	None: warming in gas-phase area	FNO_2, FNO
Total		10,100				

*The fluorine reservoir was pressurized, then opened to the N_2O_4 reactor and the F_2 was sucked through the liquid by removal of the gases above the liquid.
**The above process was accomplished twice.

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Throughout the whole experiment the reaction vessel was agitated inter-
mittently to insure thorough mixing and reaction. The only warming ob-
served was when the F_2 was passed through rapidly during steps No. V, VI,
and VIII. An overall 5 C temperature rise, corresponding to the change
in ambient temperature during the experiment, was noted. The heating was
only observed at the top of the reaction vessel above the liquid phase.
The thermocouple did not show any temperature rise in the liquid phase.
Infrared sampling indicated that some FNO was also formed, towards the
end of the experiment. A total of approximately 17 grams of F_2 was passed
through or into the liquid N_2O_4. At the end of the addition infrared ana-
lysis of the liquid phase by expansion of a portion of the liquid into an
infrared cell indicated the presence 2.9 mole percent FNO_2.

Conclusions

The experiment showed that approximately 8.5 of the 17 grams of fluorine
added were used either to completely passivate the system and to react
with any moisture in the N_2O_4 itself or were vented during the addition.
The procedure adapted near the end of the experiment showed that a fairly
rapid addition of fluorine to nitrogen tetroxide could be made without
excessive heat resulting. Occasional venting may be desired to remove
small amounts of oxygen formed from the reaction of fluorine or FNO_2 with
any water present in the NTO.

VAPOR PRESSURE AND SOLUBILITY

Apparatus Used

The apparatus used for the vapor pressure measurements consisted of a 10-
milliliter stainless steel Hoke cylinder equipped with a pressure trans-
ducer and an internal thermocouple sheathed in stainless steel. For
measurements above room temperature, the pressure transducer and the ullage
associated with it were warmed to about 5 C higher than the liquid by

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heating tapes. The total volume of the apparatus was 16.5 milliliters, and the ullage averaged about 11 milliliters. A fuller description of the equipment may be found in Ref. 4.

Vapor Pressure of FNO_2

All references in the literature to values of the vapor pressure of FNO_2 stem from the measurements made in 1932 by O. Ruff (Ref. 5), wherein he measured its vapor pressure from -155 to -72.8 C in a quartz apparatus. Although reasonable agreement has been found with the literature values in the -70 C and below range, at room temperature and above actual measured vapor pressure was twice that predicted by the equation in Ref. 5. This result is not surprising in view of the narrow range of temperatures used in the older work.

In this work, the FNO_2 was handled in a monel and Teflon high-vacuum line which had the vapor pressure measuring apparatus affixed to it. The whole system was passivated with fluorine gas and with FNO_2 itself. The FNO_2 used in the measurements was passed through a -126 C trap, where all of the impurities. were condensed and the purified compound was collected in a -196 trap. Its purity was tested by examination of its vapor pressure at -80 C, which was 540 mm (Ref. 5 reports 528 mm), and by ascertaining that it was tensiometrically homogeneous (i.e., when the free space above the liquid was doubled, the vapor pressure remained constant). The purified FNO_2 was loaded into the measuring equipment by vacuum transfer and condensation at -196 C. During the course of the measurements, the vapor pressure of the FNO_2 was periodically checked at -80 C to ascertain its purity. All measurements reported are an average of several independent determinations employing two different batches of FNO_2 purified in the manner described above. A vapor pressure equation was obtained from the data using the method of least squares. The following equation was obtained:

$$\log p_{mm} = 7.4729 - \frac{918.93}{T}$$

where

   p = pressure in mm/Hg

   T = temperature in degrees Kelvin

Physical constants derivable from this equation are: boiling point, -73.1
C (-72.4 in Ref. 5); ΔH_v, 4.20 kcal/mole; Trouton's constant, 21.0.

Vapor Pressure of FNO_2

t C	p_{mm} found	p_{mm} calculated
-78.9	543	554
-45.8	2,770	2,703
-23.1	6,410	6,291
0.0	12,800	12,860
25.2	24,300	24,740

The vapor pressure of FNO_2 at temperatures higher than 25 C was not measured
because of the limited pressure rating of the valves employed in the
equipment.

Vapor Pressure of FNO_2 and N_2O_4 Mixtures

Essentially the same procedures and precautions were taken in the measure-
ments of the vapor pressure of FNO_2 and N_2O_4 mixtures, as were described
for the case of pure FNO_2. The N_2O_4 was distilled into the apparatus,
and the amount added determined by weight difference. The FNO_2 was dis-
tilled in, and the amount added was determined by measuring the pressure
and volume of the gas. The stainless steel equipment was not completely
passivated with solutions of FNO_2 in N_2O_4. The rate of attack of the
mixture on the walls of the equipment was slow at 0 C, intermediate at
25 C, and at 50 C small quantities of noncondensable gases were always
formed during a measurement. To obtain meaningful results, the measure-
ments at 50 C were corrected for the amount of noncondensable gases

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present, determined by cooling the apparatus to -196 C immediately after
a measurement. In this way, consistent results could be obtained from
different runs; nevertheless, the accuracy of measurements at 50 C are con-
sidered to be of the order of 10 percent.

A further correction was made for the concentration of FNO_2 in the liquid
phase, taking into account the fact that the FNO_2, because of its greater
volatility, would be present in higher concentrations in the gas phase.
A computer program developed at Rocketdyne (Ref. 4) was employed to make
this correction. The results are presented in Fig. 4, 5, and 6.
It will be seen that the solution is close to ideal. The ideal and ex-
perimental curves at 50 C do not meet as the FNO_2 concentration approaches
zero due to the reaction of FNO_2 with the equipment. Henry's law constants
for FNO_2 were obtained at the temperatures 0, 25, and 50 C, and in concen-
trations ranging from 0.07 to 4.72 percent (by weight). Utilizing the
expression X_{FNO_2} k P_{FNO_2}, where X_{FNO_2} is the mole fraction of FNO_2 in
the N_2O_4 solution and P_{FNO_2} is the partial pressure of FNO_2, k's were ob-
tained equal to 7.5×10^{-5} mm^{-1} at 0 C, 6.1×10^{-5} mm^{-1} at 25 C and 6.0 x
10^{-5} mm^{-1} at 40 C. The average error of the k's obtained was $\pm 0.6 \times 10^{-5}$
mm^{-1}, standard deviation $\pm 0.8 \times 10^{-5}$ mm^{-1}, and probable error = $\pm 0.5 \times$
10^{-5} mm^{-1}.

FREEZING POINT DETERMINATION

The same apparatus was used for the freezing point determination as was
employed for the vapor pressure measurements. The melting point was de-
termined by the reverse of the cooling curve method. The material was
frozen at -196, and the temperature was measured every minute from -140
to 0 C with the thermocouple sheathed in stainless steel and immersed in
the frozen mass. When this method was employed with N_2O_4, a melting point
of -11.6 was found, which compared well with the literature value of
-11.2 (Ref. 6).

A mixture of FNO_2 and N_2O_4 was prepared, whose nominal composition was
5.45 percent by weight. The composition corrected for the FNO_2 in the
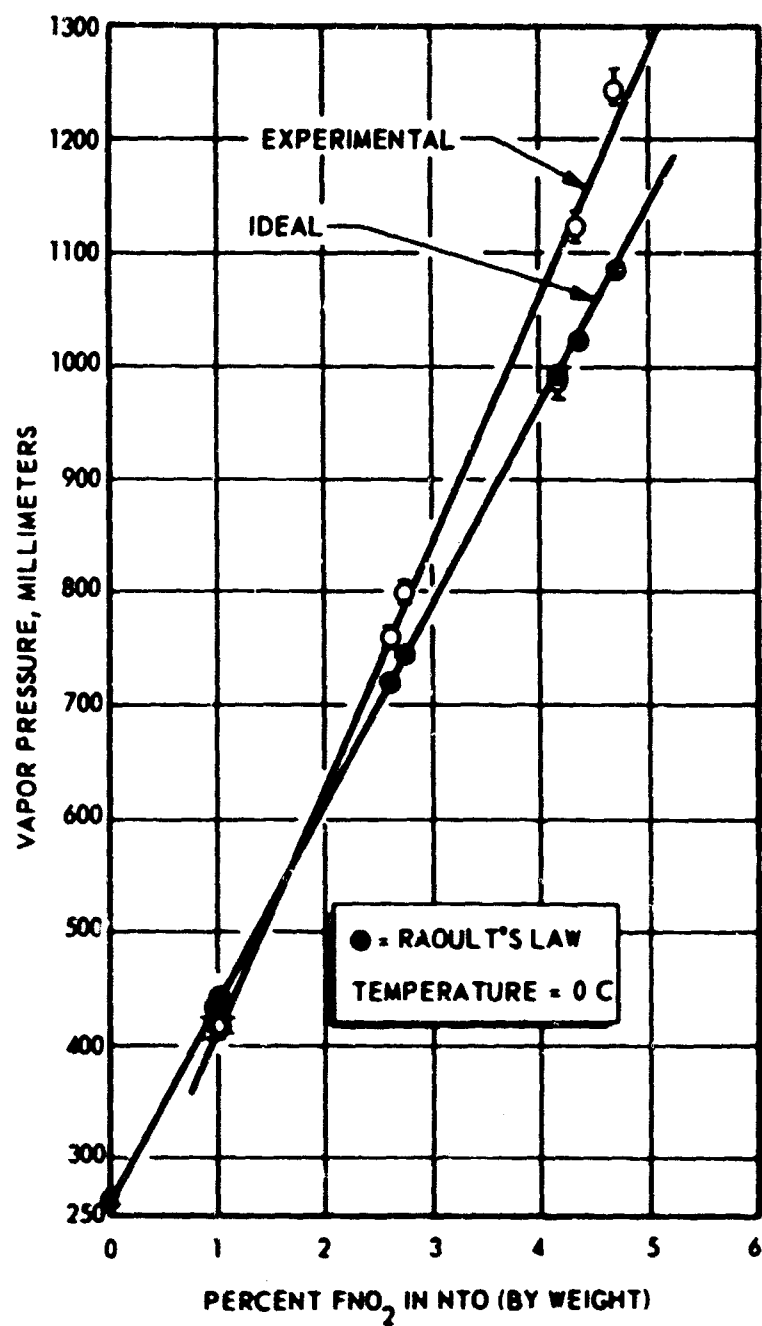vapor phase was 4.72 percent, and its melting point determined by the same

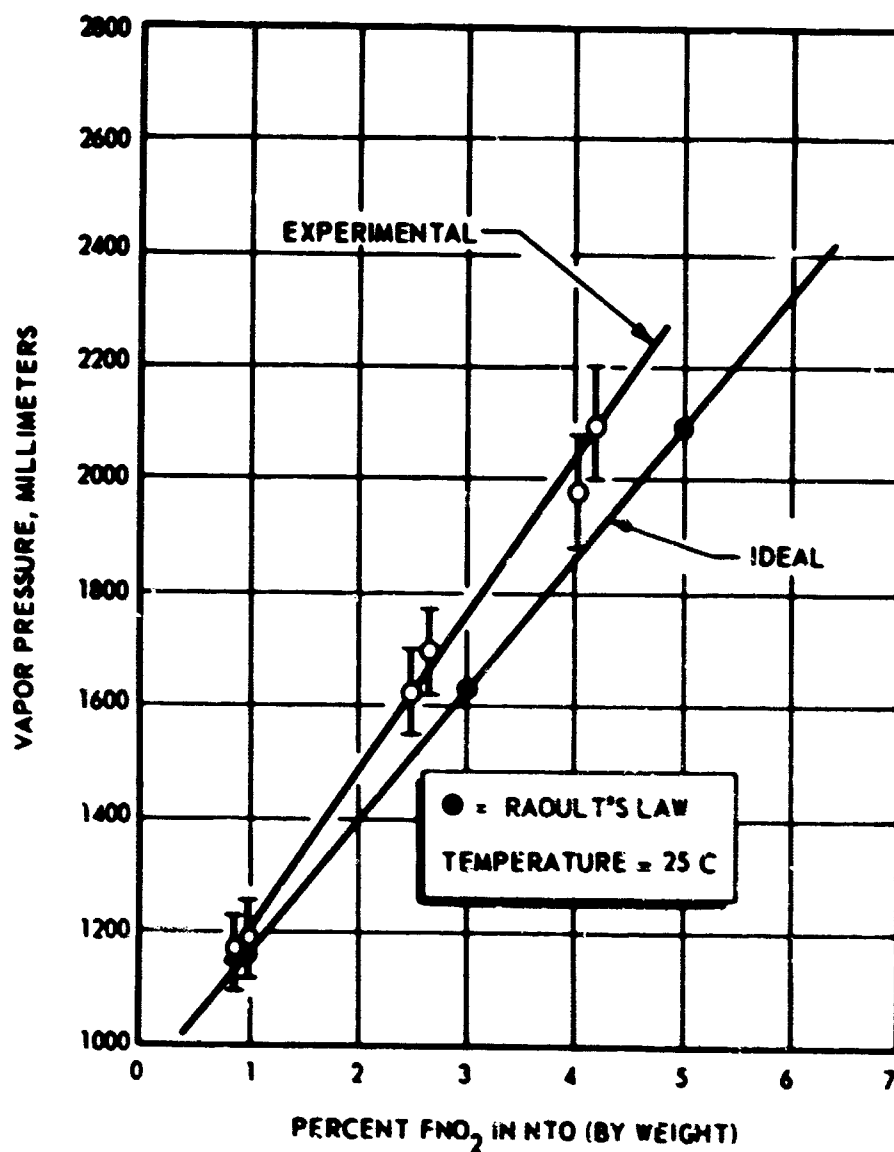Figure 4. Vapor Pressures of NTO-FNO₂ Solutions, 0 C
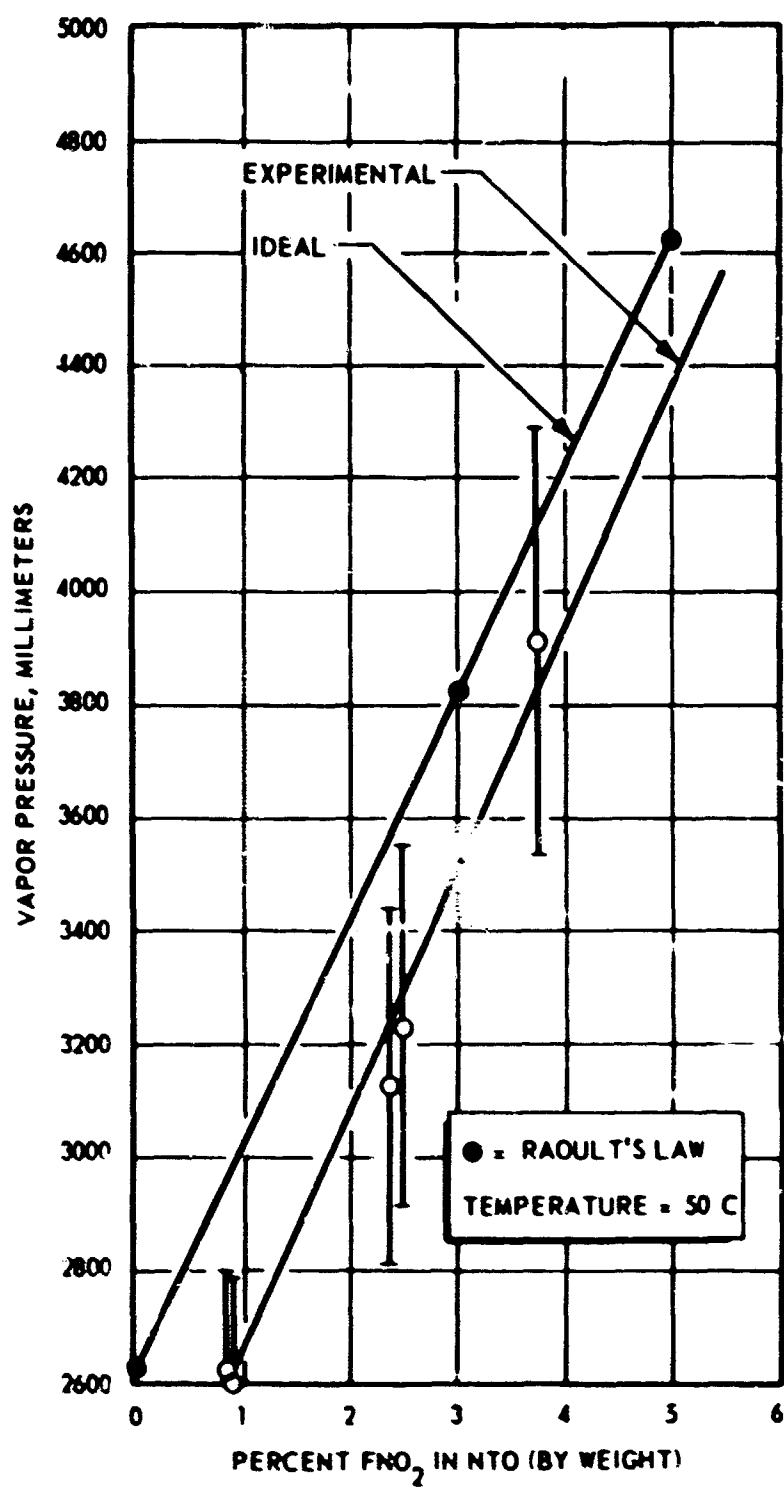
Figure 5. Vapor Pressures of NTO-FNO₂ Solutions, 25 C

Figure 6. Vapor Pressures of NTO-FNO₂ Solutions, 50 C

method as used for N_2O_4. A good plateau was not found in the plot of temperature vs time; a plot of the first differential of the data gave a melting point for the mixture of -12.0 C. N_2O_4 has a molar freezing point depression constant of 3.6 C/mole additive/1000 gms of solvent. Hence, a freezing point depression of 2.6 C would be expected for a 4.72 weight percent solution. It is considered that with the present apparatus this is the best result that can be obtained; for higher precision a truly passive apparatus is needed in which the mixture can be continually and thoroughly mixed as the freezing point is approached.

SUMMARY

To successfully and meaningfully conduct the engine evaluation of Phase I, it was necessary to develop analytical chemical methods for the complete analysis of NTO, F_3NO, FNO_2 NTO + F_3NO, and NTO + FNO_2. No single chemical technique is available which will successfully analyze all of these compounds; therefore, a combination of methods was required for a complete analysis. The procedures that were developed are described immediately infra.

EXPERIMENTAL

Nuclear Magnetic Resonance

The n.m.r. method for the determination of protons in NTO (Ref. 7) has been used to check the water equivalent of the NTO samples used in Phase I. F^{19} n.m.r. has been used to confirm the formation of FNO_2 by the reaction between F_2 and NTO, and the formation of HF by the reactions of F_3NO and FNO_2 with the HNO_3 present in NTO.

Infrared

The thermal stability of NTO + F_3NO was followed mainly by IR analysis, and the results are given elsewhere in this report. A calibration for FNO_2 in NTO has been obtained in the infrared region by using the intensity of the 12.18-micron band of FNO_2 as a quantitative measure of the FNO_2 content. The calibration curve is shown in Fig. 7. This method was used to show that the reaction of F_2 and NTO did produce FNO_2 in sufficient quantity to yield INTO. A spectrum of NTO + FNO_2 is shown in Fig. 8. Figure 9 shows the calibration curve for the 2.51-micron band of HF that is used to determine the HF formed when a fluorine oxidizer is added to NTO containing some water.
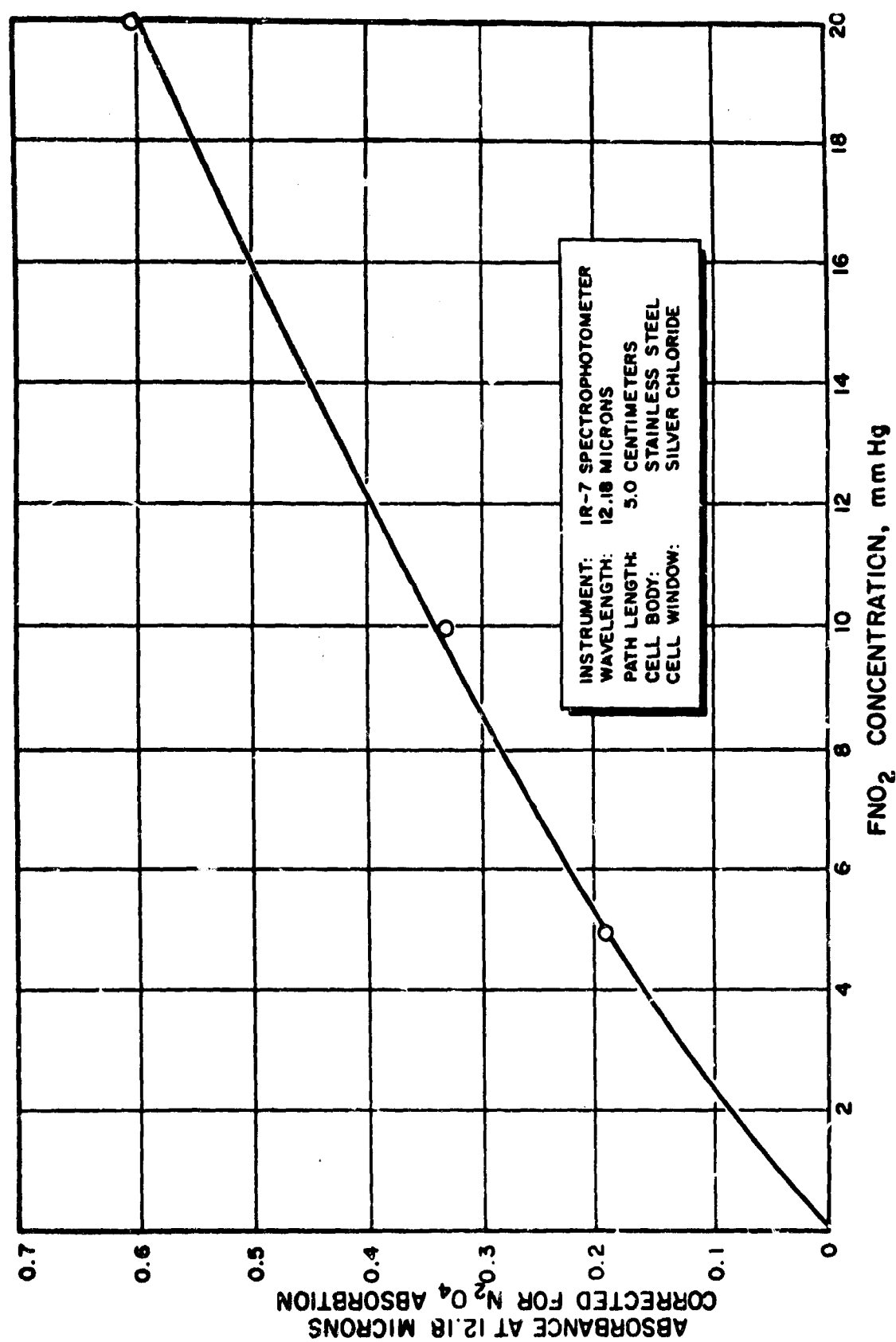
41

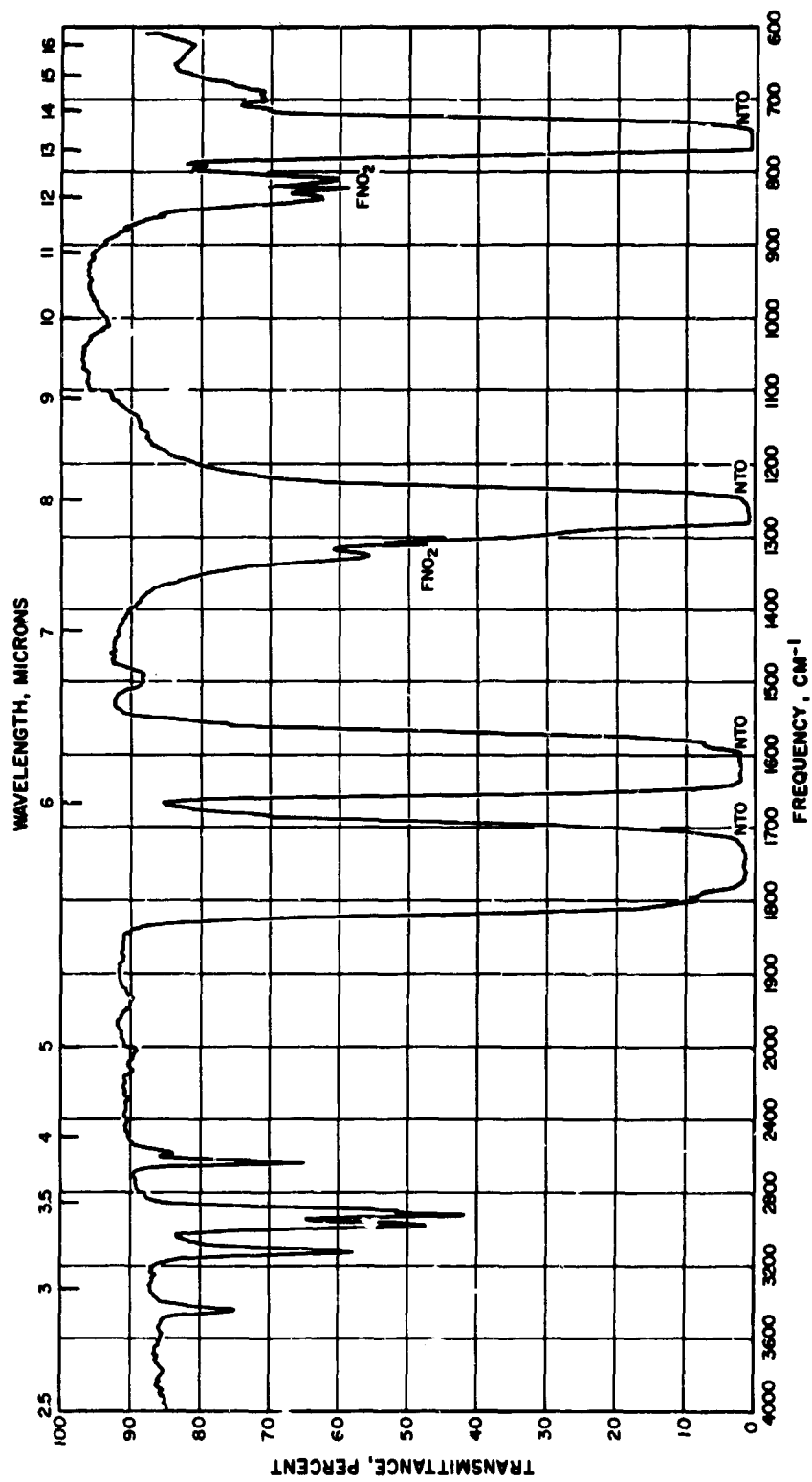Figure 7. Spectrophotometer Calibration Curve for FNO_2 in N_2O_4

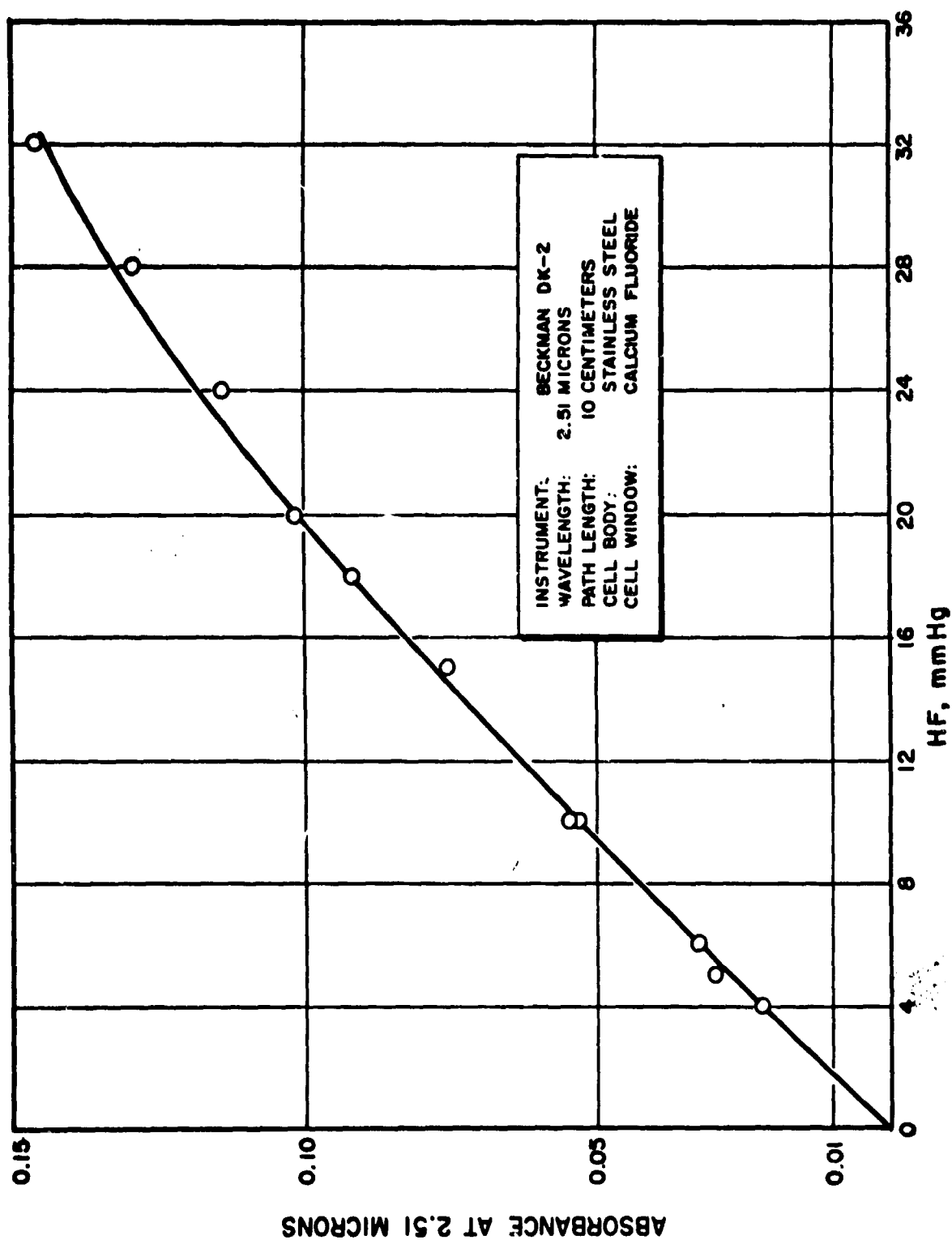Figure 8. Infrared Spectrum of NTO + FNO$_2$

Figure 9. Spectrophotometer Calibration Curve for HF

Gas Chromatography

There have been many unsuccessful attempts over the past decade to analyze nitrogen oxides by gas chromatographic methods (Ref. 8 and 9). These attempts have been made with both gas/liquid and gas/solid columns.

The use of gas/liquid chromatography, which utilizes an organic substrate to achieve separation, was precluded by the extreme reactivity of NTO, which will react with almost any organic substrate used in chromatography. Conventional gas/solid chromatography uses materials such as silica gel, molecular sieve, alumina, etc., to achieve separation by surface adsorption. However, most of the materials mentioned exhibit a high degree of polarity. Attempts to analyze nitrogen oxides using such materials resulted in broadtailing peaks, which precluded the possibility of using this approach as a basis for a quantitative analytical technique.

During this program, a gas chromatographic technique was developed that will successfully analyze F_3NO, NTO, and INTO samples for F_3NO, NO_2, N_2O, NO, O_2, and N_2. The method consists of trapping the NO_2 (and possibly any HF, N_2O, or CO_2) at -80 or -126 C on an AlF_3 column, passing the remaining gas mixture over either a 4-percent halocarbon wax on porous glass or a Linde Sieve 5A column, and then into a thermal conductivity detector. The NO_2-containing AlF_3 column then is warmed to ambient temperature and the evolved gas is passed directly through the same detector. Using the halocarbon wax on porous glass column, NO + O_2 + N_2, F_3NO, N_2) (if in high enough concentrations), and NO_2 can be determined. F_3NO, O_2, N_2, NO, and NO_2 can be determined by using the Linde Sieve 5A column. For a complete analysis, two samples must be run, one with each column.

An interesting aspect of the gas chromotographic analysis of NTO is that NO will pass through the -80 or -126 C trap rather than being retained as N_2O_3. The NO passes through the trap because at the sample pressure used (200 mm), the $NO + NO_2 \rightleftharpoons N_2O_3$ equilibrium lies far to the left and, when the mixture is passed through the trap, its residence time is insufficient for the equilibrium to shift to the right. This was checked

by determining chromatographically the NO content of two samples of N_2O_4 containing 0.57 ±0.05 weight percent NO (as determined by the proposed NASA procurement specification, PPD-2). The NO contents found chromatographically were 0.59 and 0.61 weight percent.

Water Equivalency

The most straightforward method of ascertaining the efficiency of drying NTO by adding a fluorine oxidizer would be to measure the water equivalency of a portion of an NTO sample by a standard military specification procedure and to similarly measure the water equivalency of a second portion of the same NTO sample to which a fluorine oxidizer had been added. Unfortunately, the HF formed by the reaction of a fluorine oxidizer with wet NTO reacts with the glass window of the phase separation Military Specification apparatus. This reactivity precludes using that equipment. Instead, it has been necessary to fabricate of an unreactive material an approximate copy of the Turner bulb apparatus formerly called out as a military specification.

An aluminum flask has been constructed for the purpose of obtaining water equivalent data from samples of INTO. The flask is shown in Fig. 10. High purity aluminum 1100 and aluminum 3003-0 were chosen for construction materials because of their weldability and corrosion resistivity. The total weight of the flask is about 70 grams. Passivation of the aluminum container was accomplished by exposing it to 50-percent HF for 1 week and to N_2O_4 for 1-week. Water contents of N_2O_4 determined with this apparatus agreed to within 0.01 weight percent with those determined with a glass Turner bulb apparatus.
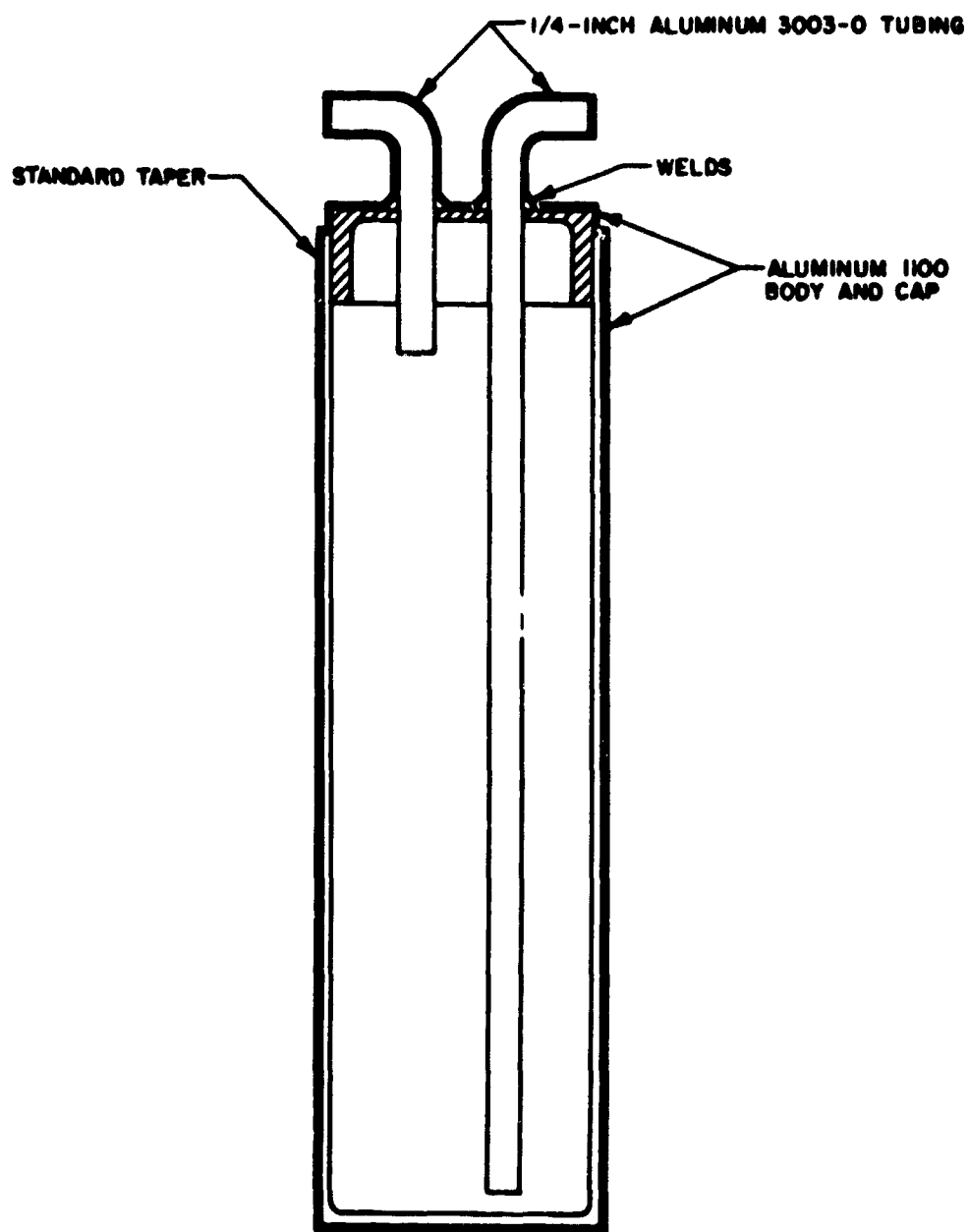
Figure 10. Aluminum Flask (Actual Size)

Mass Spectrometric

Mass spectrometric analysis was used to check the purity of F_3NO. The analysis revealed F_3NO (90.8 percent), O_2 (4.7 percent), NO_2 (2.3 percent), N_2O (1.1 percent), and CO_2 (0.9 percent). This was in substantial agreement with the gas chromatographic results. Mass spectormetry is not expected to be useful for the analysis of INTO since the $M/E = 30$ peak is common to too many of the constituents.

SUMMARY

PHASE I: ENGINEERING EVALUATION

INTO has been evaluated to determine its storability, its corrosive effects upon typical materials of construction, its transferability, and its possible field preparation. In addition, its vapor pressure, freezing point, and conductivity have been determined.

It has been found that INTO is storable at 70 C in stainless steel, aluminum, and nickel containers with no apparent change in composition for at least 6 months. Therefore, storage in containers made of any of these materials should be feasible.

Thirty-day studies have been completed at ambient temperature and at 70 C of corrosion of iron and aluminum alloys exposed to INTO and NTO. Twenty-month studies of corrosion of these alloys at ambient temperature are now in progress. On the assumption that the results of the 20-month tests will not conflict with the data already obtained, the following conclusions can be drawn: (1) wet NTO will corrode aluminum and iron alloys at 70 C; (2) INTO will passivate aluminum alloys at ambient and at elevated temperature; (3) HF will passivate both aluminum and iron alloys but only significantly (visually apparent) at elevated temperatures; (4) INTO does not significantly passivate iron alloys; (5) passivation layers on aluminum are much heavier with NTO + FNO_2 than with NTO + HF; (6) although passivation layers are not visually apparent, 300 series stainless-steel alloys withstand corrosion far better than 1018 carbon steel, 440 C stainless steel, and AM 350 SCT; (7) 2014 and 2024 aluminum alloys form thinner and more adherent passivation layers than do 7075, 6061, Tens 50; (8) the passivation layers react on exposure to (moist) air. It is recommended that systems designed to use the INTO oxidizer be constructed of alloys such as the 300 series stainless steels or 2014 or 2024 aluminum which have been found to behave significantly better when exposed to the propellant.

The effects upon nonmetals of INTO as compared to NTO have also been studied. It was found that Kel-F, Teflon, Kynar, butyl rubber, and Viton A are comparably effected by both compositions.

The conductivities of FNO_2 + wet and dry NTO, wet and dry NTO, and dry NTO + HF have been measured. Only a relatively small change in solution conductivity was noted. It is therefore not anticipated that INTO will present more galvanic corrosion problems than does NTO.

The effects of intermittently flowing INTO made from wet and dry NTO through 25- and 100-pound valves for a 2-week period have been investigated. No deterrent effects upon valve performance were observed. The use of INTO is therefore not expected to contribute to valve failure problems.

A method for preparing INTO under field conditions has been developed. This method consists of bubbling F_2 through liquid propellant grade NTO at ambient temperature. The reaction has been shown to proceed smoothly and no difficulties are anticipated in scaling up the operation.

Measurements of the vapor pressures and freezing points of INTO solutions have been completed. No unusually large variations were discovered in either phenomenon. Henry's Law constants for FNO_2 were measured and found to be 7.5×10^{-5} mm^{-1} at 0 C, 6.1×10^{-5} mm^{-1} at 25 C, and 6.0×10^{-5} mm^{-1} at 40 C. It is not anticipated that any major changes will be required in systems designed for use with NTO, due to the substitution of INTO for NTO as a result of the changes in vapor pressure and freezing point.

Reclamation of wet NTO as demonstrated by a reduction in water equivalent has been conclusively demonstrated by addition of fluorine or FNO_2. It has also been shown that INTO may be transferred in a closed system without appreciable loss of FNO_2. The FNO_2 content was found to be somewhat lowered after transfer because of the filling of the ullage of the container into which the INTO was being transferred by the INTO vapors. A slow drop in FNO_2 content of the INTO was also noted until the new container had completely passivated. To minimize these effects, transfers of INTO should be made under the following conditions: (1) in closed

systems, (2) the container into which the INTO is being transferred should be filled as near to full as possible to minimize ullage, and (3) the FNO_2 content of the solution being transferred should be somewhat higher than than desired in the final container.

PHASE II: ANALYTICAL STUDIES

Analytical chemical methods have been developed which allow INTO to be analyzed for F_3NO, FNO_2, NTO, NO, N_2O, HF, O_2, N_2, and H_2O. F_3NO, FNO_2, and HF have been determined by F^{19} n.m.r. H_2O has been determined by H^1 n.m.r. and by using an aluminum Turner bulb apparatus. F_3NO, NTO, NO, N_2O, O_2, and N_2 have been determined by gas chromatography. F_3NO, FNO_2, and HF have been determined by quantitative infrared spectrophotometry. Techniques for performing these analyses are described in the body of this report.

RECOMMENDATIONS

The encouraging results obtained on the INTO program suggest the further development of INTO as an operational propellant. Additional engineering properties will be evaluated on Contract F04611-67-C-0008. Further work has been proposed in response to RFQ F04611-67-R-0059.

In addition to these efforts, INTO should, of course, be test fired. Furthermore, before any system is constructed in which INTO is to be used as the oxidizer, determinations should be made of the effects of storing all of the specific construction materials of the system in contact with INTO under mission duty conditions.

REFERENCES

1. AFRPL-TR-65-51: Final Report, Preparation and Characterization of a New High-Energy Oxidizer, Contract No. AF04(611)-9563, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, April 1965, CONFIDENTIAL.

2. Addison, C. C., J. Allen, H. C. Bolton, and J. Lewis, J. Chem. Soc., 1951, 1289-94.

3. Lange, N. A.: "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1946.

4. AFRPL-TR-65-125, Final Report, Physico-Chemical Characterization of High-Energy Storable Propellants, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, May 1965, CONFIDENTIAL.

5. Ruff, O., W. Menzel, and W. Neumann, Z. anorg. allgem. Chem., 208, 293 (1932).

6. Giauque, W. F., and J. D. Kemp, J. Chem. Phys., 6, 40 (1938).

7. Sutton, N. V., H. E. Dubb, R. E. Bell, I. Lysyj, and B. C. Neale, Advances in Chemistry Series, 54, 231-5 (1966).

8. Greene, S. A., and H. Pust, Anal Chem., 30, 1039 (1958).

9. Hoffmann, E. R., and I. Lysyj, Michrochem. J., VI, 45 (1962).

APPENDIX A

CORROSION TEST DATA
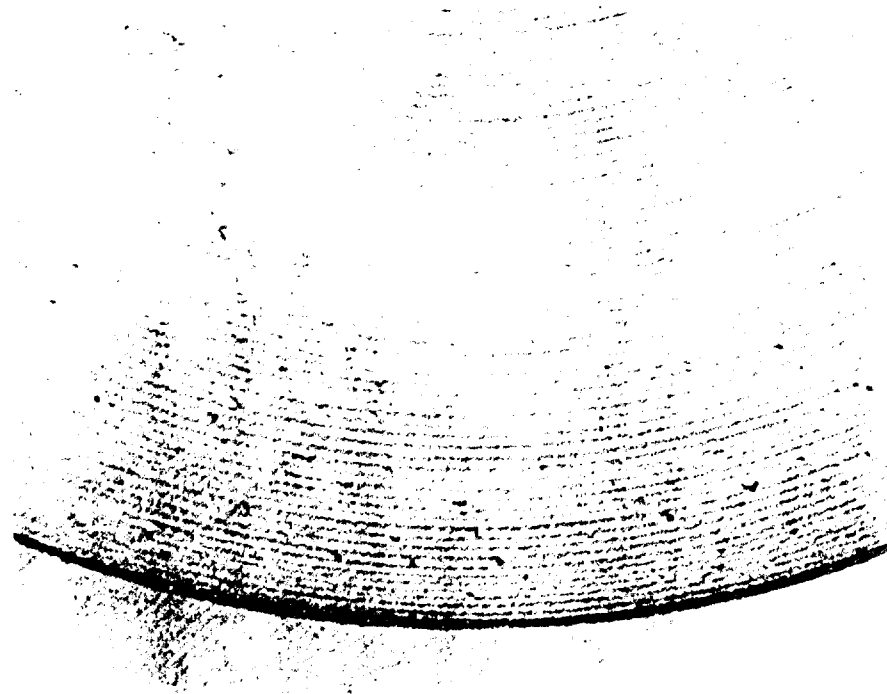
a. 440 Stainless Steel
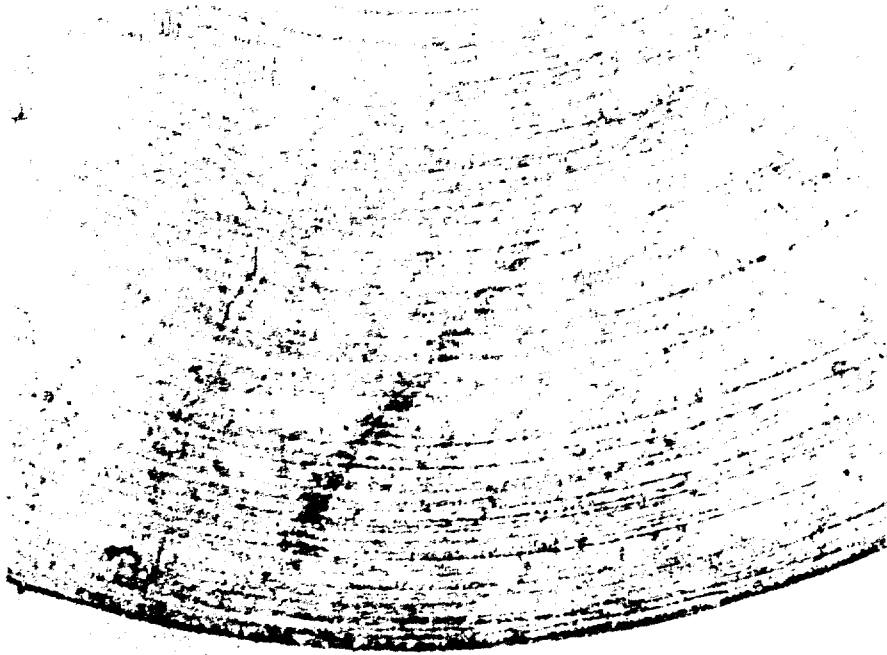
b. 1018 Carbon Steel

Figure A-1. Ferrous Control Specimens
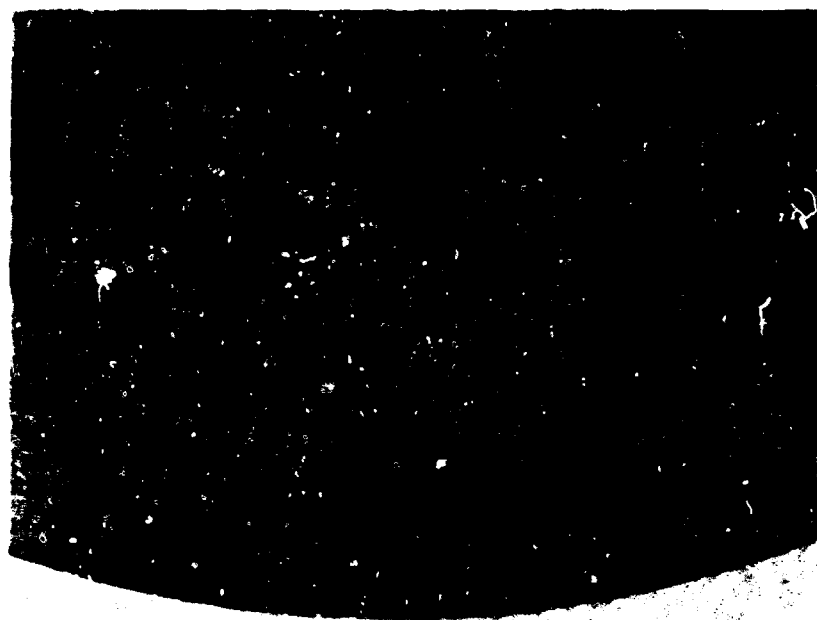
a. 440 Stainless Steel
(Vapor Phase)
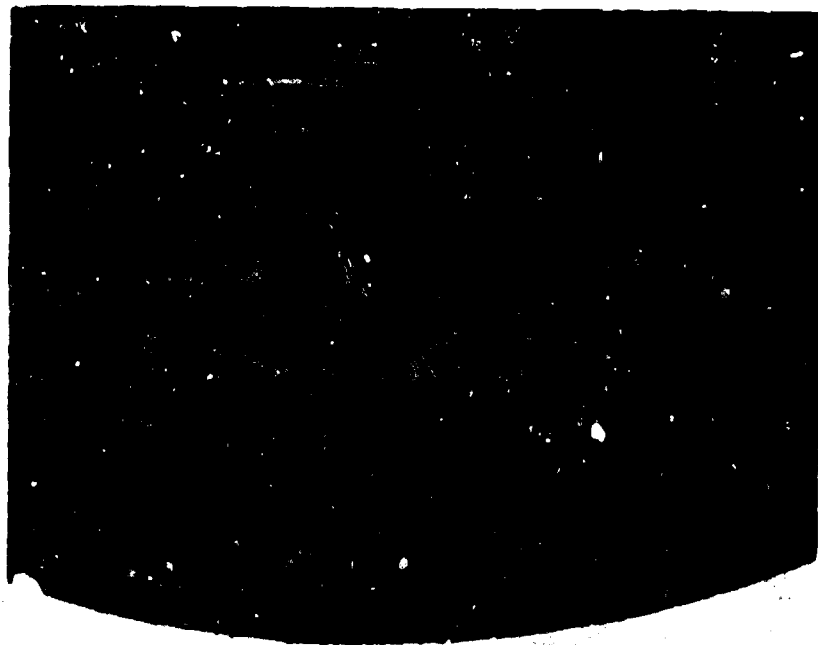
b. 1018 Carbon Steel
(Liquid Phase)

Figure A-2.   Ferrous Specimens Exposed to Dry NTO,
Ambient Temperature
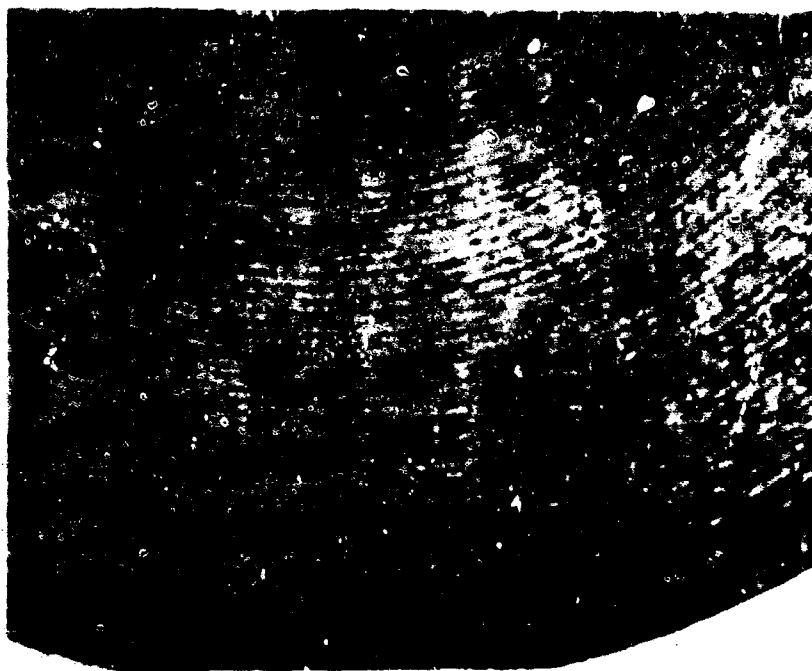
a. 440 Stainless Steel
   (Liquid Phase)
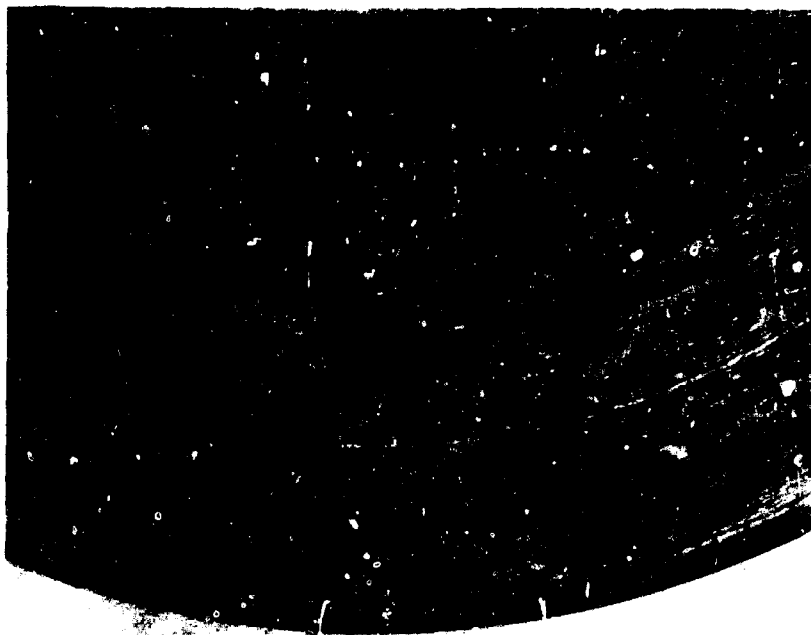
b. 1018 Carbon Steel
   (Vapor Phase)

Figure A-3. Ferrous Specimens Exposed to Wet NTO,
Ambient Temperature

a. 440 Stainless Steel
   (Vapor Phase)

b. 1018 Carbon Steel
   (Liquid Phase)

Figure A-4. Ferrous Specimens Exposed to Dry $N_2O + FNO_2$,
Ambient Temperature

a. 440 Liquid Phase
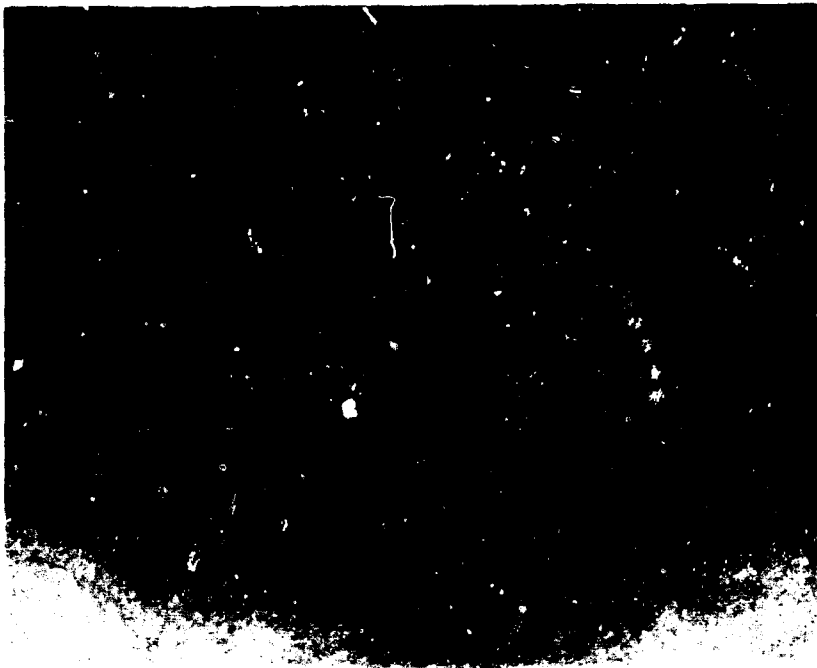
b. 1018 Vapor Phase

Figure A-5. Ferrous Specimens Exposed to Wet NTO + FNO$_2$, Ambient Temperature
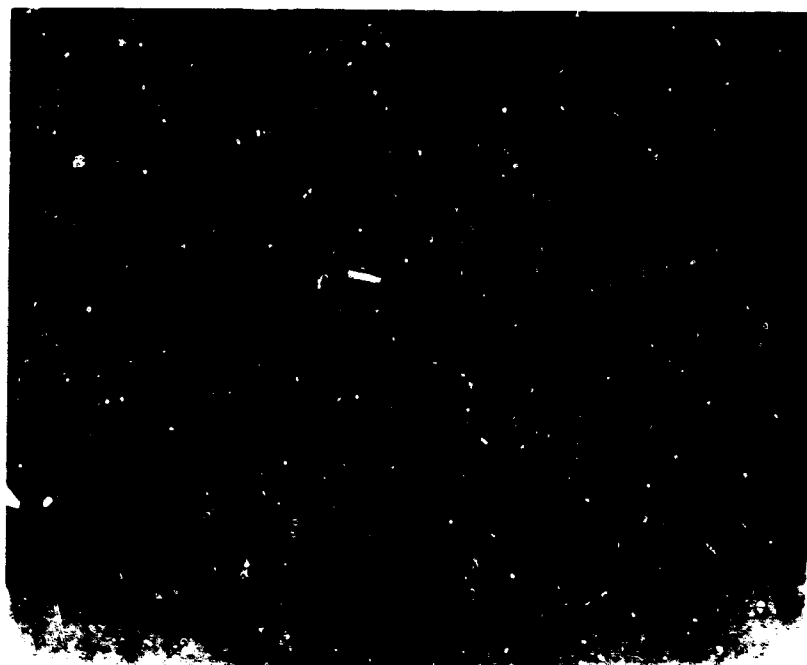
a. 440 Stainless Steel
   (Liquid Phase)
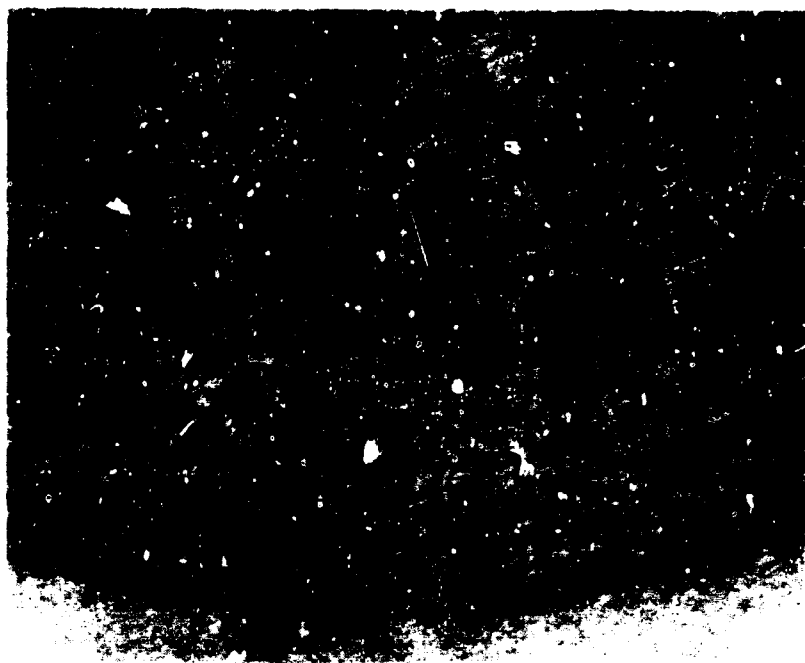
b. 1018 Carbon Steel
   (Vapor Phase)

Figure A-6. Ferrous Specimens Exposed to Dry NTO + HF
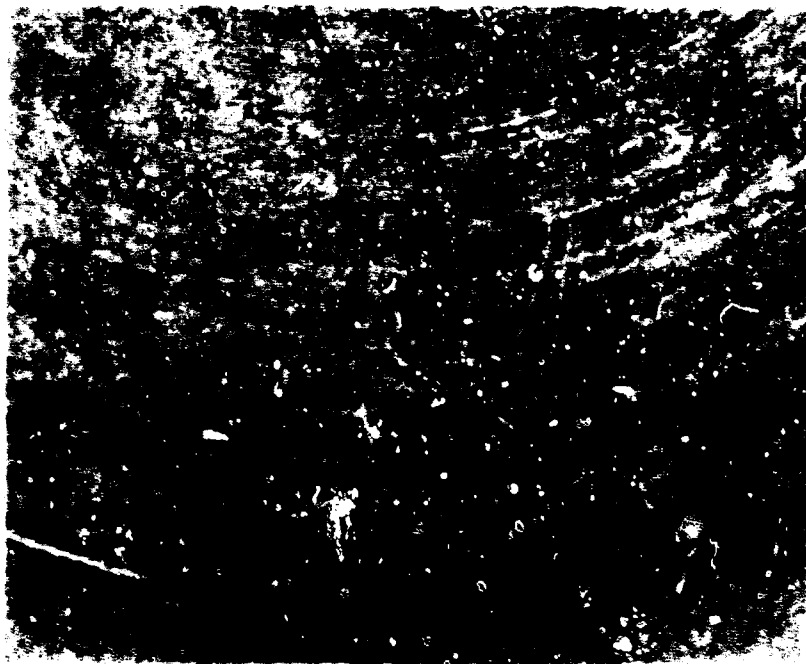
b. TENS-50 Aluminum

a. 6061 Aluminum

Figure A-7. Aluminum Control Specimens

a. 6061 Aluminum
    (Liquid Phase)

b. TENS-50 Aluminum
    (Liquid Phase)

Figure A-8.   Aluminum Specimens Exposed to Dry NTO,
              Ambient Temperature

A-9
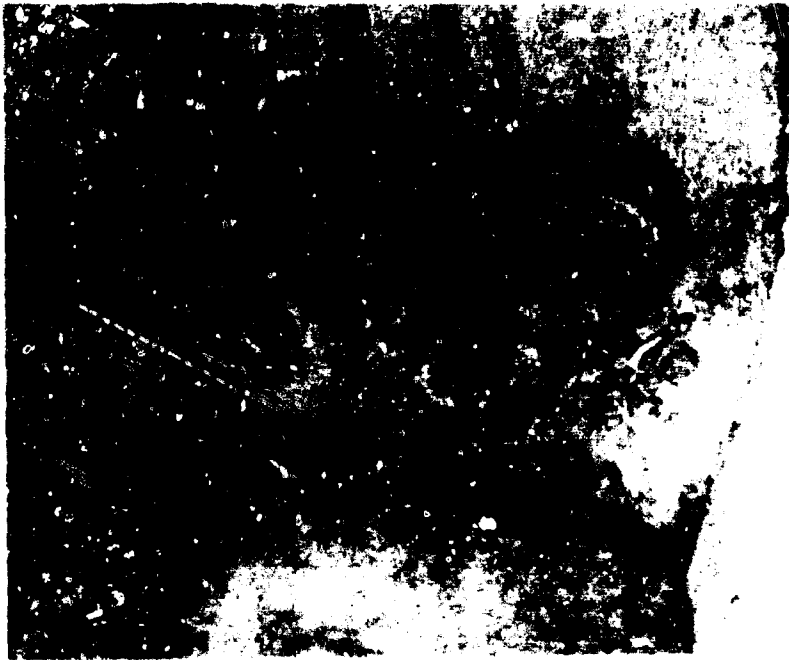
b. TENS-50 Aluminum
   (Vapor Phase)

a. 6061 Aluminum
   (Vapor Phase)

Figure A-9. Aluminum Specimens Exposed to Wet NTO,
             Ambient Temperature

A-10
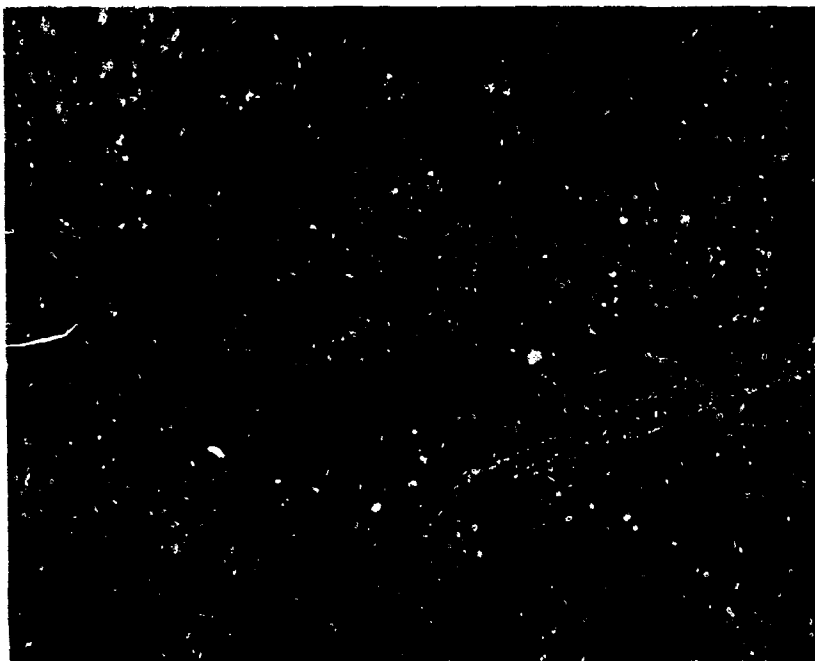
a. 6061 Liquid Phase

b. TENS-50 Liquid Phase

Figure A-10. Aluminum Specimens Exposed to Dry NTO + FNO_2, Ambient Temperature
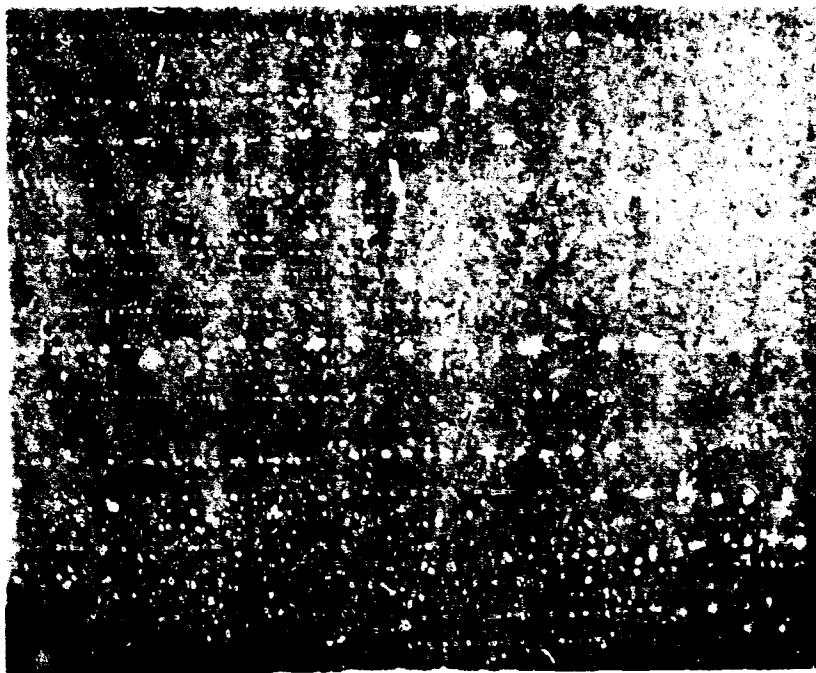
a. 6061 Liquid Phase
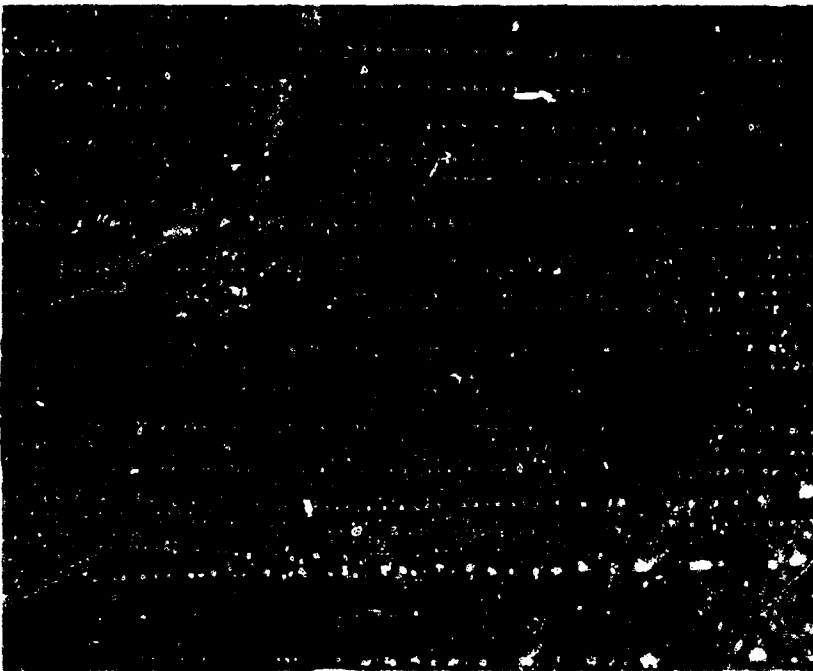
b. TENS-50 Vapor Phase

Figure A-11. Aluminum Specimens Exposed to Wet NTO + FNO$_2$, Ambient Temperature

b. TENS-50 Aluminum
(Liquid Phase)
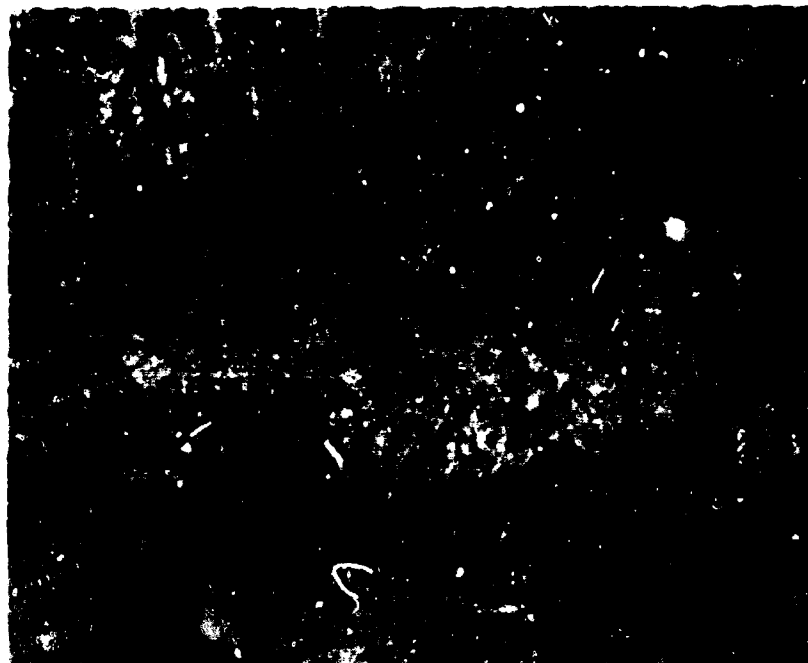
a. 6061 Aluminum
(Vapor Phase)

Figure A-12. Aluminum Specimens Exposed to Dry MTO + HF,
Ambient Temperature

A-13
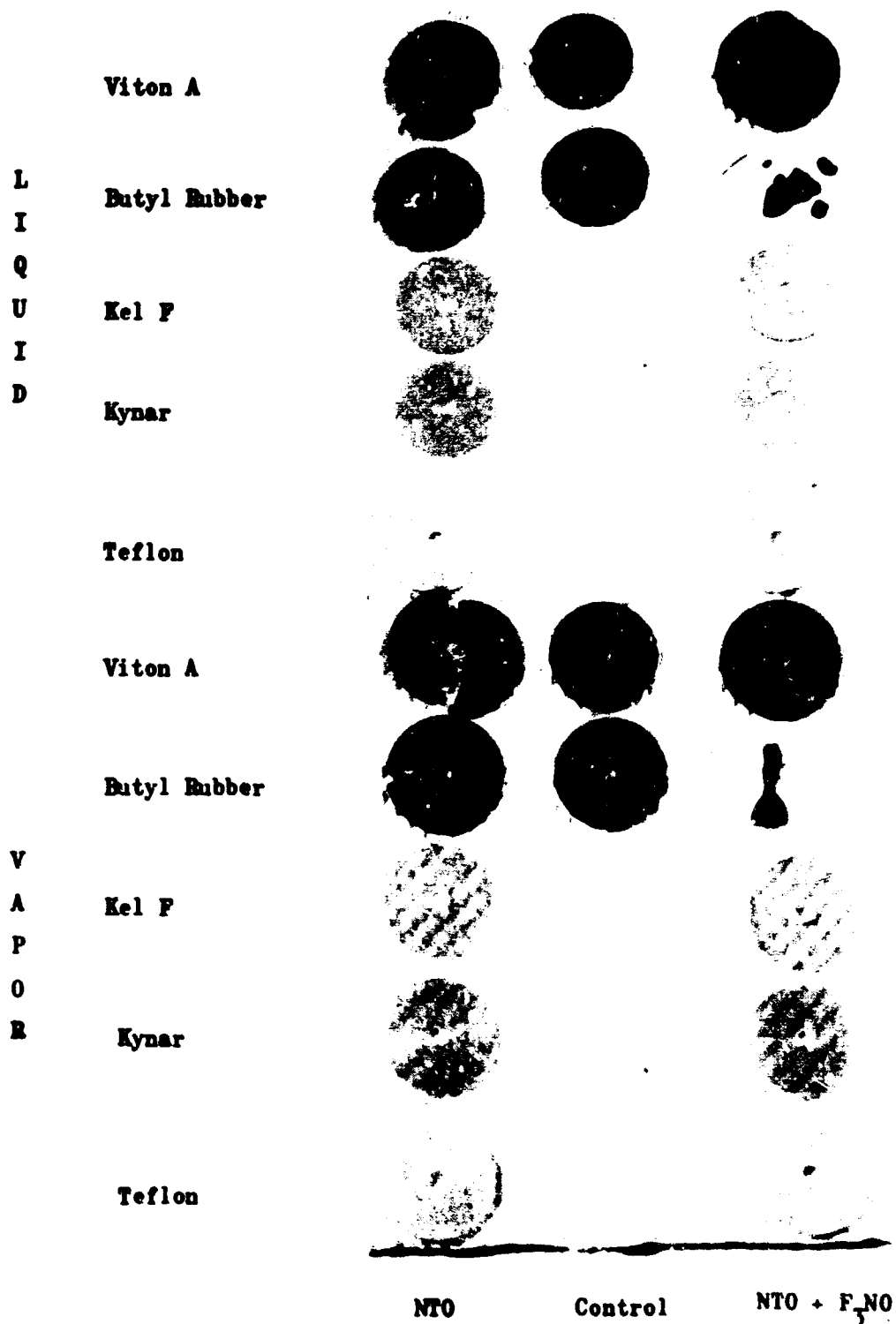
Figure A-13. Seven-Day NTO and NTO + F₃NO Test Nonmetals Tests

A-14
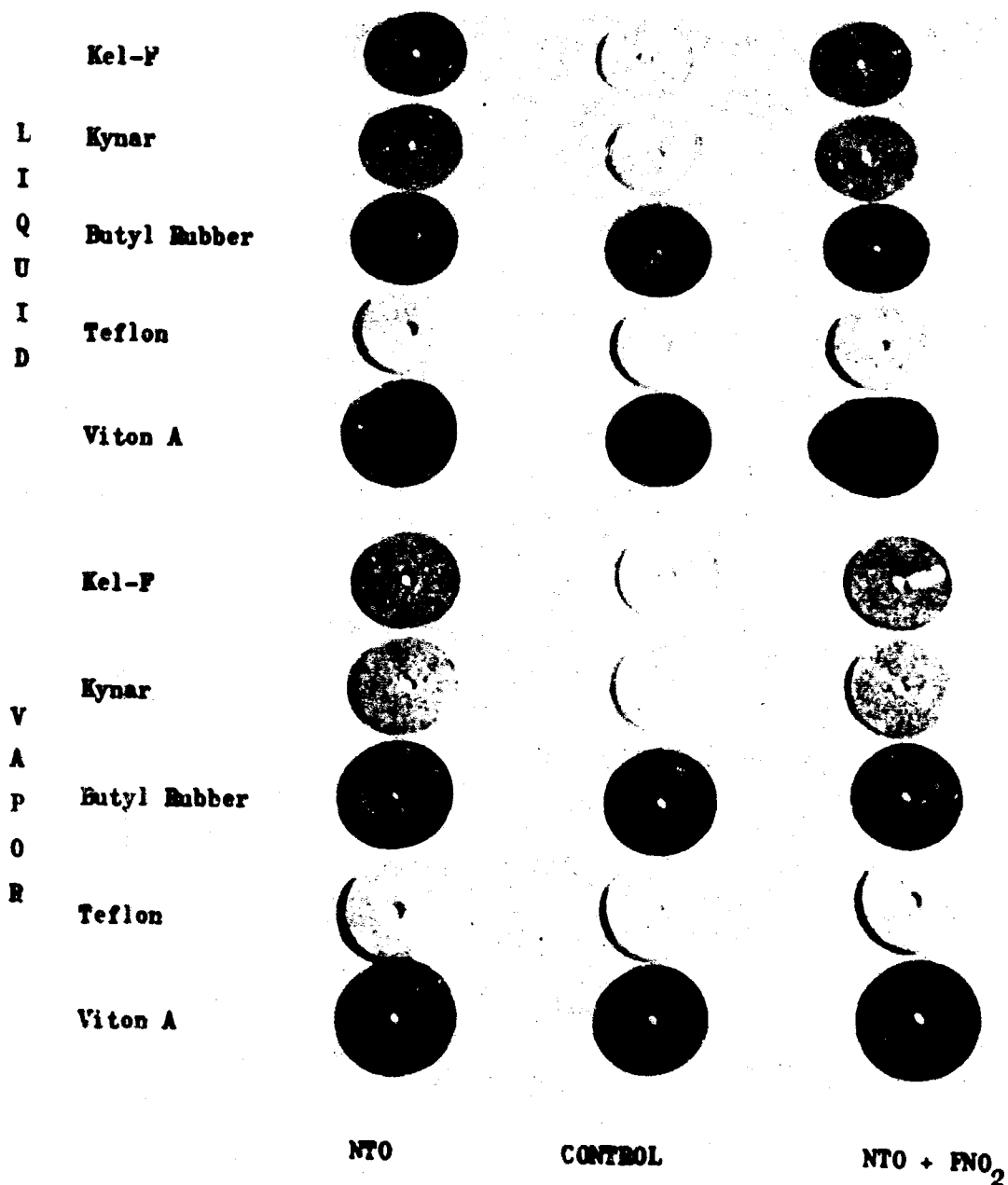
Figure A-14. Seven Day NTO and NTO + FNO_2 Nonmetals Tests
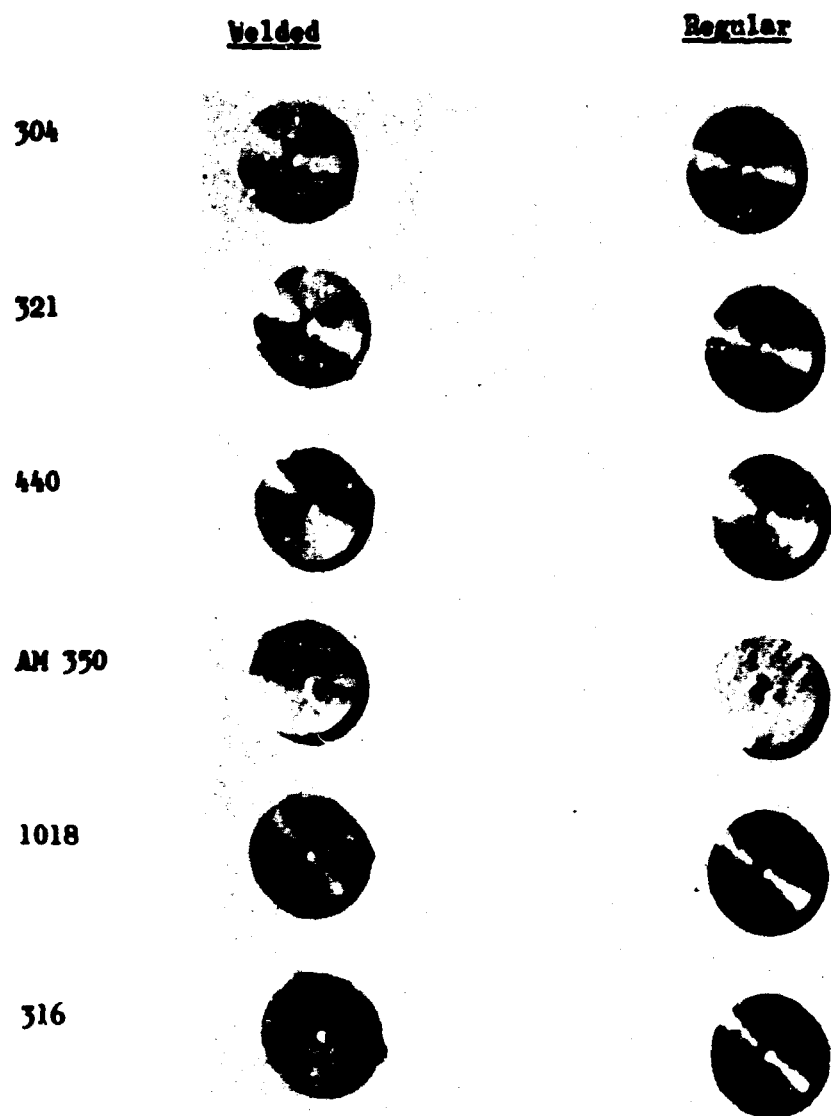
Figure A- 15   Ferrous Control Specimens

Welded   Regular

6061

7075 (Not Weldable)

TENS-50

2014
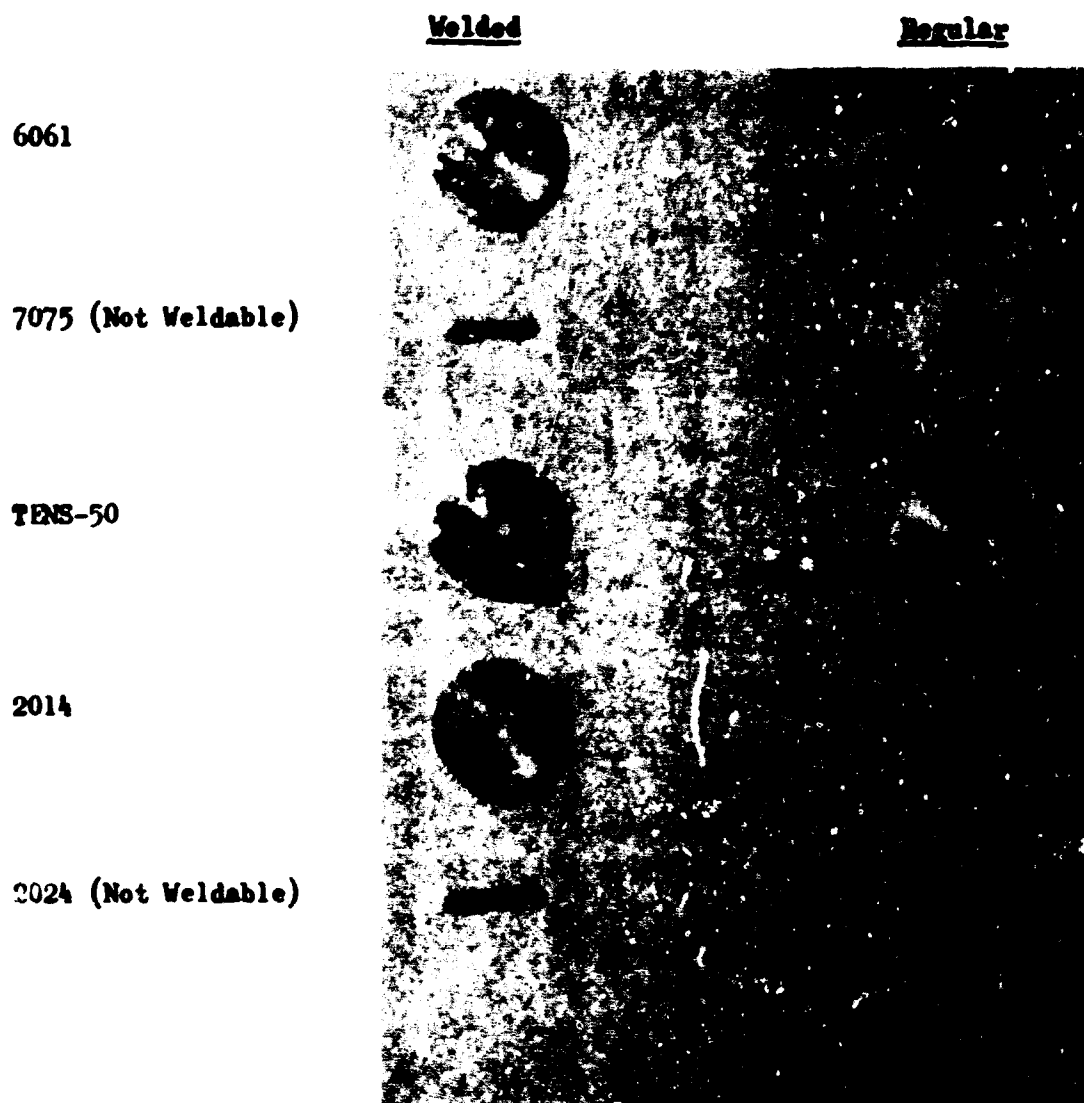
2024 (Not Weldable)

Figure A-16. Aluminum Control Specimens

Figure A-17. Dry INTO 30-Day Ambient Aluminum Specimens

	Welded	Regular

6061

7075 (Not Weldable)

L
I
Q
U   TENS-50
I
D

2014

2024 (Not Weldable)

6061

V   7075 (Not Weldable)
A
P
O   TENS-50
R

2014
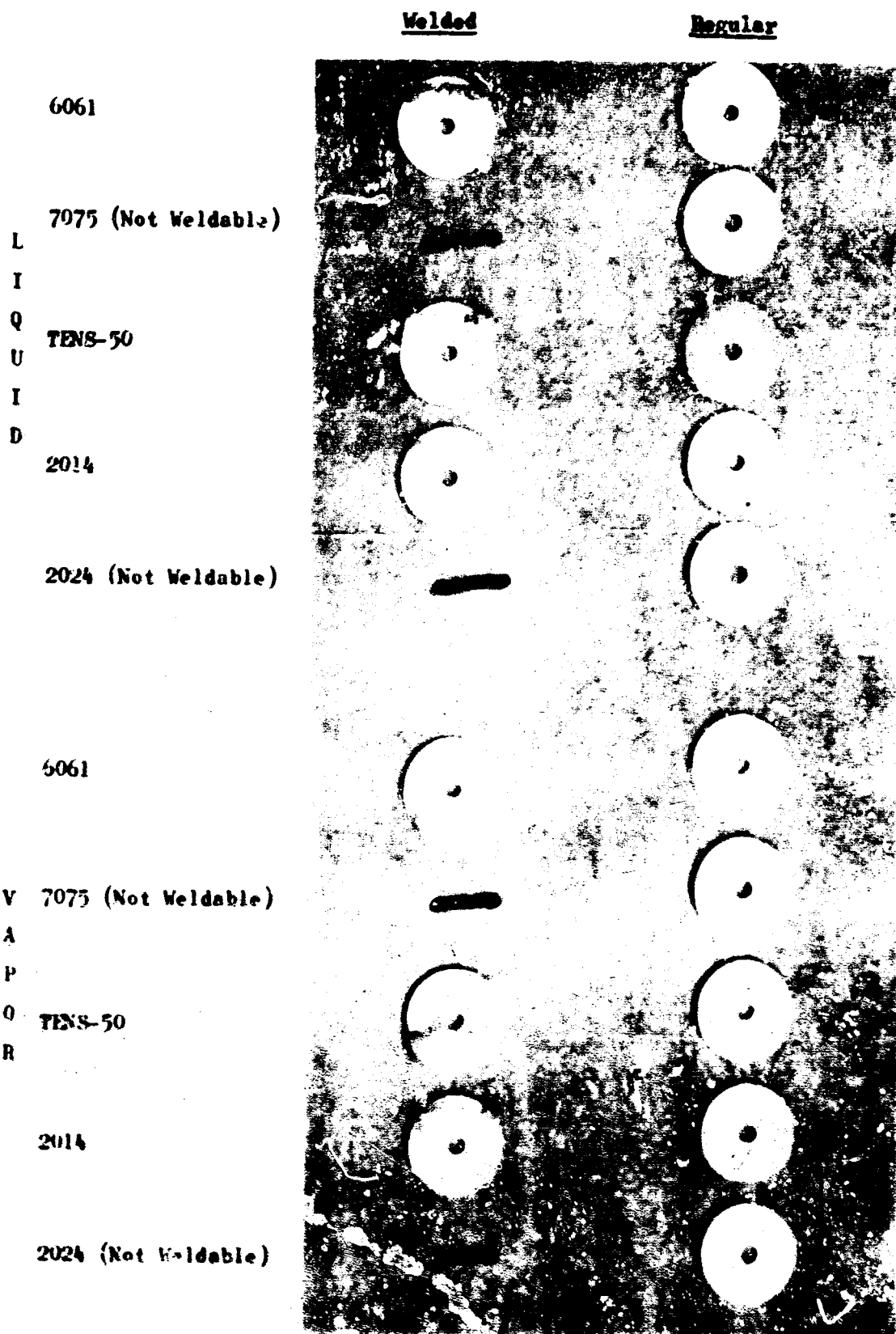
2024 (Not Weldable)

Figure A-18.   Dry INTO 30-Day High-Temperature Aluminum Specimens

A-19

Welded   Regular

6061

7075 (Not Weldable)

L
I
Q
U   TENS-50
I
D   2014

2024 (Not Weldable)

6061

7075 (Not Weldable)

V
A
P   TENS-50
O
R   2014

2024 (Not Weldable)

Figure A-19.   Wet INTO 30-Day Ambient Aluminum Specimens.
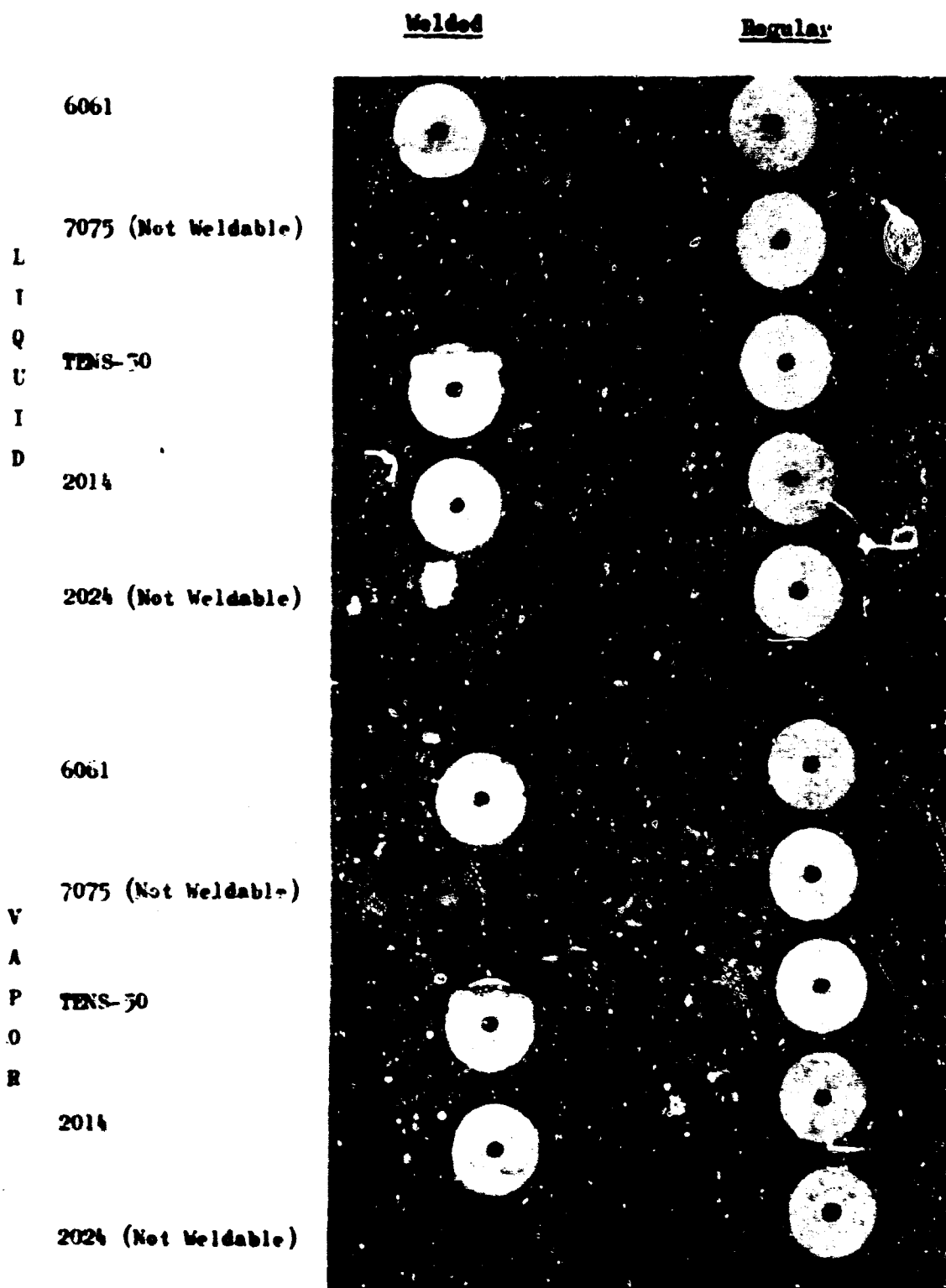
Figure A-20. Wet INTO 30-Day High-Temperature Aluminum Specimens
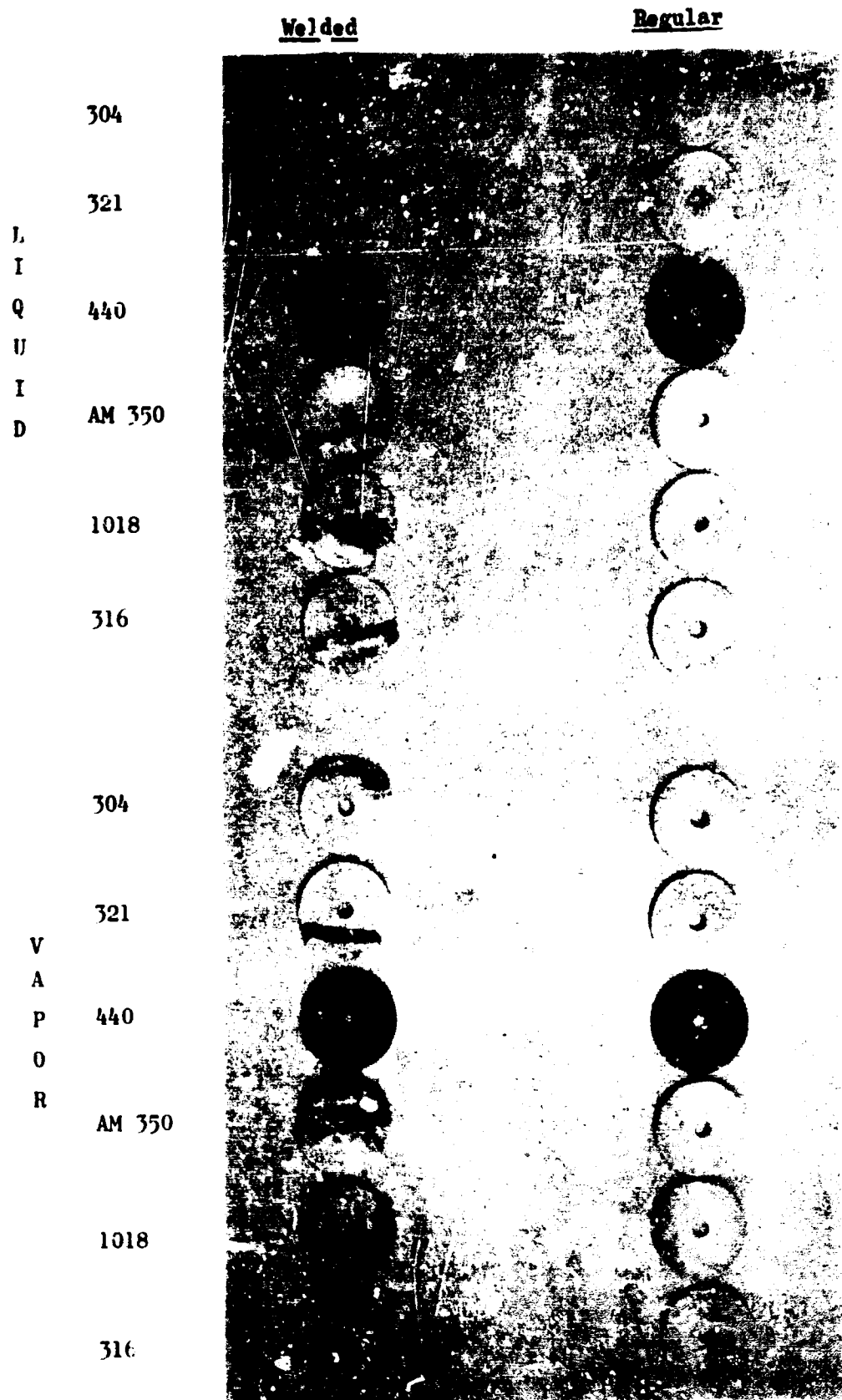
Figure A-21. Wet INTO 30-Day High-Temperature Ferrous Specimens

A-22

	Welded	Regular

6061

7075 (Not Weldable)

L
I
Q   TENS-50
U
I
D   2014

2024 (Not Weldable)

6061

7075 (Not Weldable)

V
A
P   TENS-50
0
R

2014

2024 (Not Weldable)
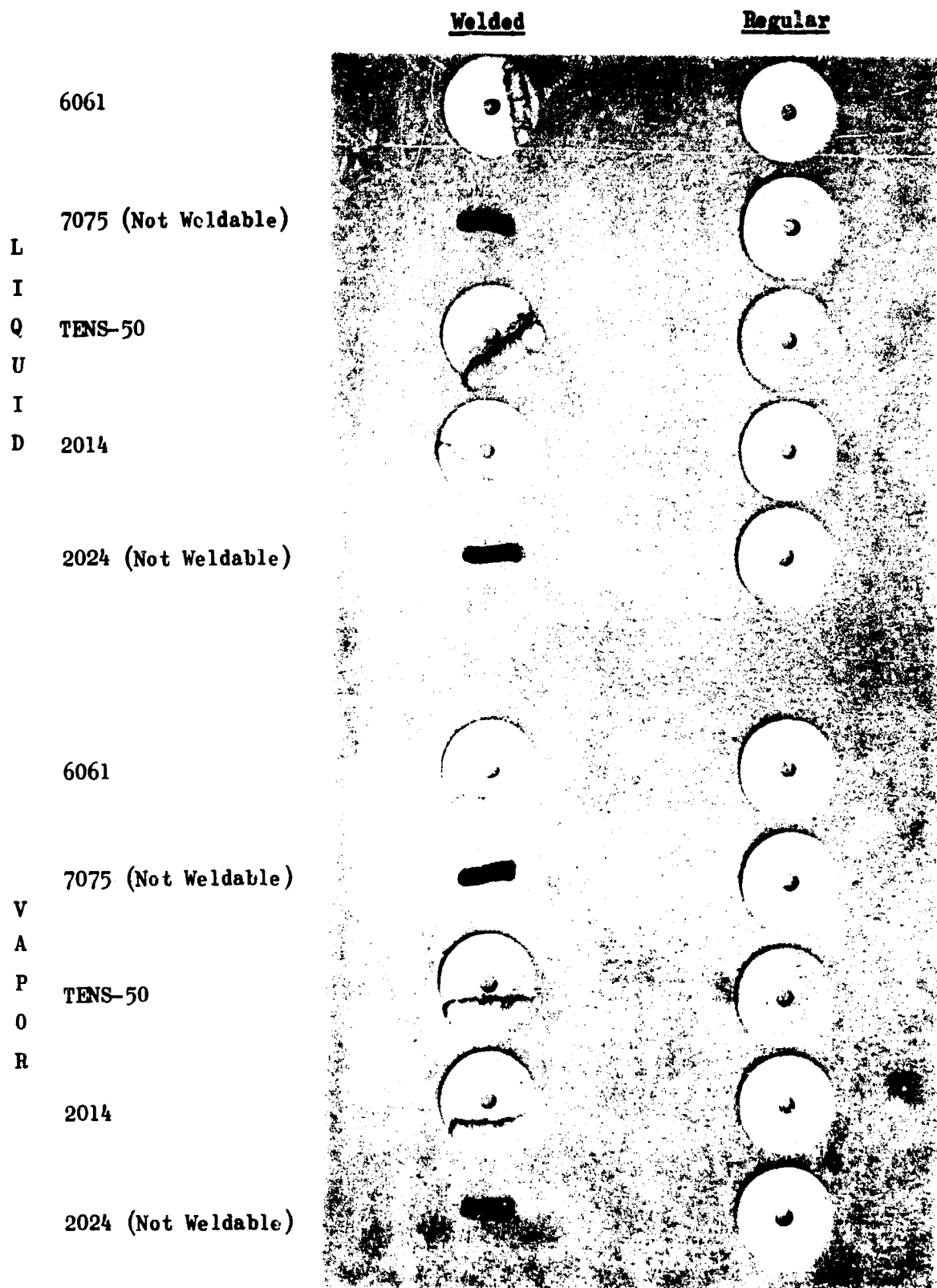
Figure A-22.   Dry NTO + HF 30-Day High-Temperature Aluminum Specimens
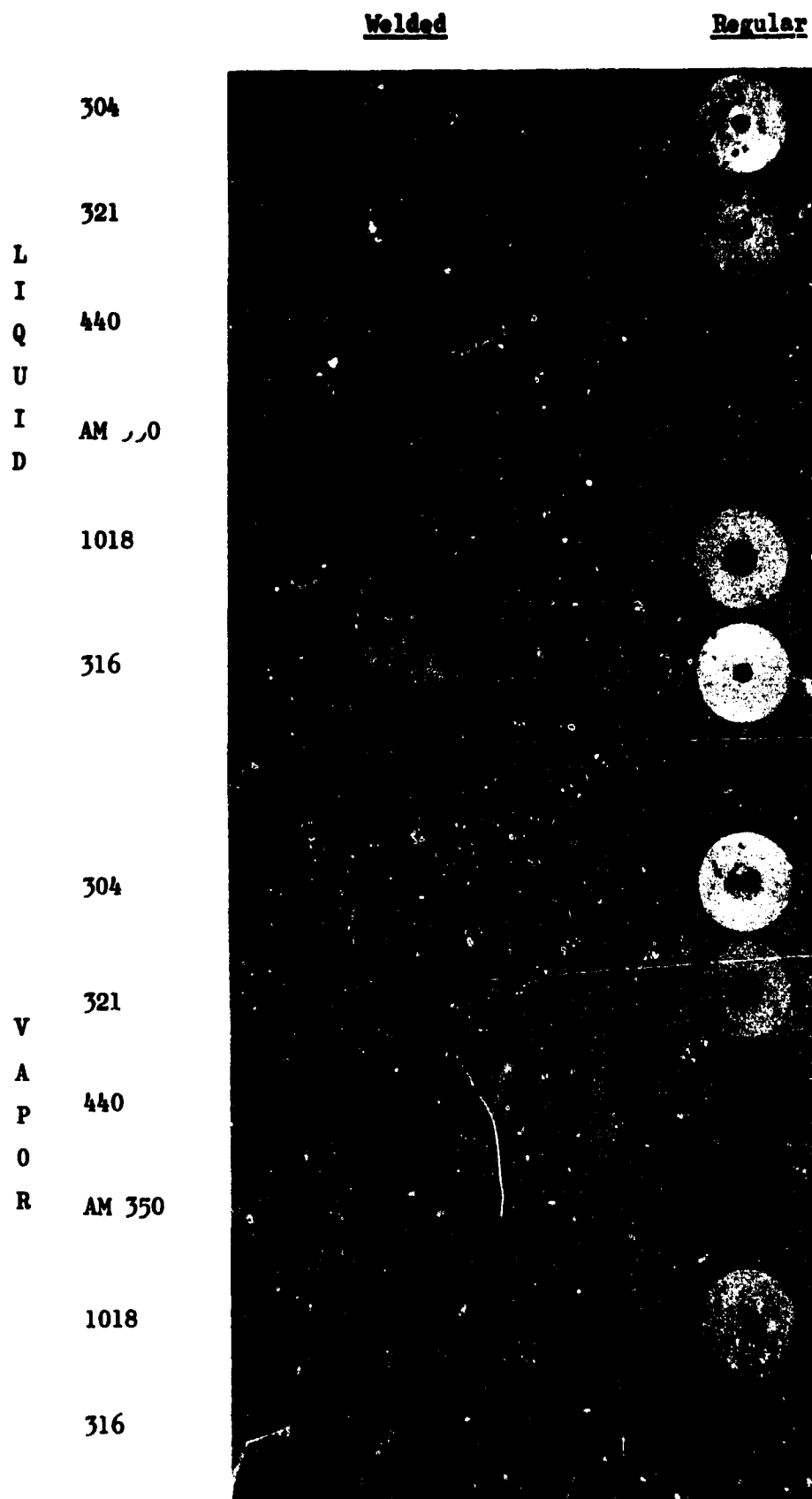
Figure A-23. Dry NTO + HF 30-Day High-Temperature Ferrous Specimens

TABLE A-1

NTO TESTS WITH NONMETALS

Material	Weight Before, grams	Weight After, grams	Weight Change After 72 Hours, grams	Percent Weight* Change After 72 Hours	Percent Weight* Change After 240 Hours	Comments
Liquid Phase						
Kel-F	0.5235	0.5468	0.0233	4.4	3.5	Surface slightly softer in both solutions and both phases; color changed to light amber; no apparent size change
Kynar	0.4413	0.4578	0.0165	3.7	2.4	Color changed to light green; no apparent size change
Butyl Rubber	0.3183	0.3428	0.0245	7.7	5.4	Extreme swelling to 1-3/4 times original size as observed immediately upon removal; surface slightly spongier than control specimen; no apparent color change
Teflon	0.5462	0.5480	0.0018	0.3	0.2	No apparent change in size or surface hardness; color changed to buff but returned to original color upon extended exposure to atmosphere (240 hours)
Viton A	0.5940	0.6341	0.0401	6.7	7.2	Extreme swelling to approximately twice original size observed upon removal from bomb; reduced to 1.1 original size in 50 minutes upon exposure to atmosphere; greater swelling, cracking, and warping in liquid phase than in vapor phase; slight reduction in elasticity
Vapor Phase						
Kel-F	0.5318	0.5554	0.0236	4.4	3.5	Color changed to light amber; surface slightly softened; no apparent size change
Kynar	0.4577	0.4542	0.0165	3.8	2.5	No apparent size change; color changed to light green; very slight surface softening
Butyl Rubber	0.3383	0.3690	0.0307	9.1	6.6	Extreme swelling observed upon removal from bomb; no apparent color change; surface appeared spongier than central specimen
Teflon	0.5557	0.5573	0.0016	0.3	0.2	Color changed to buff but returned to normal upon extended exposure to atmosphere (240 hours)
Viton A	0.5740	0.6185	0.0445	7.7	8.5	Extreme swelling to about twice original size upon removal from bomb; returned to 1.1 original size after 30-minutes exposure to atmosphere; no apparent color change; slight reduction in elasticity

* Percent weight change based on original weight

TABLE A-2

SEVEN-DAY COMPATIBILITY TEST OF NONMETALS WITH NTO + FNO$_2$

Material	Weight Before, grams	Weight After, grams	Weight Change After 72 Hours, grams	Percent Weight* Change After 72 Hours	Percent Weight* Change After 240 Hours	Comments
Liquid Phase						
Kel-F	0.5322	0.5562	0.0240	4.5	3.6	Surface slightly softer in both solutions and in both phases after test; color after test, light amber; no apparent size change
Kynar	0.4336	0.4496	0.0160	3.7	2.4	Surface slightly softer but not as evident as Kel-F; color changed to light green; no apparent size change
Butyl Rubber	0.3077	0.3296	0.0219	7.1	4.8	Exhibits a slight sponginess compared to control specimen; characteristics similar in liquid and vapor phase; NTO and NTO + FNO2 extreme swelling observed immediately upon removal (1-3/4 times original size)
Teflon	0.5484	0.5498	0.0014	0.3	0.07	No apparent change in surface hardness or size; color changed to buff; after extended exposure to atmosphere, color changed back to original
Viton A	0.5810	0.5731	-0.0079	-1.4	-2.5	Extreme swelling to nearly twice original size observed immediately; upon removal from test bomb, reduced to 1.1 original size after 30-minutes exposure to atmosphere; slightly greater warping, cracking, and reduction in elasticity in NTO + FNO$_2$ than in NTO
Vapor Phase						
Kel-F	0.5167	0.5400	0.0233	4.5	3.6	Changed color to light amber; surface slightly softer than control specimen; no apparent change in size
Kynar	0.4362	0.4526	0.0164	3.8	2.4	Color changed to light green; no apparent change in size; very slight softening of surface
Butyl Rubber	0.3170	0.3428	0.0258	8.1	6.0	Extreme swelling observed immediately after removal from bomb; surface spongier than control specimen; no apparent change in color
Teflon	0.5490	0.5506	0.0016	0.3	0.1	No apparent change in surface softness or size; color changed to buff but returned to original color after extended exposure to atmosphere (240 hours)
Viton A	0.6092	0.6499	0.0407	6.7	6.2	Extreme swelling to nearly twice original size observed immediately; upon removal from test bomb; reduced to 1.1 original size after 30-minutes exposure to atmosphere; reduction in elasticity as in liquid phase; less warping and cracking than in liquid phase; no apparent color change

*Percent weight change based on original weight

TABLE A-3

WEIGHT CHANGES OF SPECIMENS EXPOSED TO DRY NTO
FOR 30 DAYS AT AMBIENT TEMPERATURE

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
		Ferrous Specimens	
304 L	+0.0001	+0.006	Weight changes were approximately equal for all specimens.
316	+0.0002	−0.010	Welded specimens exhibited smaller weight decreases than nonwelded specimens.
321	+0.0001	+0.006	Liquid- and Vapor-phase welded specimens exhibited no weight changes.
AM 350	0	0	The liquid-phase nonwelded specimen showed an abnormal weight change and was discarded; vapor-phase nonwelded and liquid-phase welded specimen showed no weight change.
440	−0.0002	−0.009	The liquid-phase welded specimens showed no weight change. The vapor-phase welded specimen showed the smallest weight change.
1018	+0.0004	+0.011	The liquid-phase nonwelded specimen showed the smallest weight change.
		Aluminum Specimens	
TENS-50	−0.0002	−0.025	None
2014	+0.0001	+0.024	The vapor-phase welded specimen showed a large negative weight gain whereas all others were positive. It was discarded in averaging.

TABLE A-3
(Concluded)

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
2024	-0.0004	-0.055	The vapor-phase specimen showed three times the weight loss of liquid-phase specimen.
6061	-0.0005	-0.067	The vapor-phase welded specimen showed much larger weight decrease than others.
7075	+0.0004	+0.037	The vapor-phase specimen was discarded because it showed a large negative weight loss probably caused by dirt in a machining groove noted before the test.

TABLE A-4

WEIGHT CHANGES OF SPECIMENS EXPOSED TO WET NTO
FOR 30 DAYS AT AMBIENT TEMPERATURE

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
Ferrous Specimens			
304 L	+0.0002	+0.006	Weight changes were approximately equal for all specimens.
316	−0.0002	−0.010	Weight changes were approximately equal for all specimens.
321	−0.0002	−0.010	Weight changes were approximately equal for all specimens
AM 350	−0.0001	−0.003	The liquid-phase welded specimen showed no weight change. The vapor phase-specimens showed a weight decrease. The liquid-phase nonwelded specimen showed a weight gain.
440	−0.006	−0.027	The vapor-phase weight losses were approximately four times those of the liquid phase.
1018	−0.0001	−0.006	The vapor-phase welded specimen was the only specimen to show a weight gain. The weight loss of the vapor-phase nonwelded specimen was four times that of liquid-phase specimens.
Aluminum Specimens			
TENS-50	+0.0001	+0.019	The vapor-phase welded specimen showed no weight change. The vapor-phase nonwelded specimen showed greater change than the others.

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
2014	0	0	Nonwelded specimens exhibited a slight weight increase. The vapor-phase welded specimen showed no weight change.
2024	-0.0002	-0.030	The vapor-phase specimen showed significant weight loss. The liquid-phase specimen showed no change.
6061	0	0	All samples except the liquid-phase welded specimen showed no weight change.
7075	+0.0002	+0.014	The liquid-phase specimen showed weight gain. The vapor-phase specimen showed a weight loss.

TABLE A-5

WEIGHT CHANGES OF SPECIMENS EXPOSED TO DRY NTO FOR 30 DAYS AT 70 C

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
Ferrous Specimens			
304L	+0.0001	+0.004	None
316	-0.0001	-0.006	Vapor-phase weight losses were greater than those of the liquid-phase
321	+0.0002	+0.008	None
AM 350	+0.0001	+0.004	None
440	+0.0016	+0.076	Vapor-phase specimens showed slight weight losses whereas liquid-phase specimens showed significant gains
1018	+0.0008	+0.030	Liquid-phase specimens showed greater weight increases than vapor-phase specimens
Aluminum Specimens			
TENS-50	-0.0012	-0.132	None
2014	+0.0011	+0.146	Vapor-phase nonwelded specimen showed weight gain about 10 times those of others
2024	-0.0011	-0.139	Liquid-phase specimen showed weight loss twice that of vapor-phase specimen
6061	-0.007	-0.098	All weight losses were about equal
7075	-0.0002	-0.014	Liquid-phase specimen showed no weight change

TABLE A-6

WEIGHT CHANGES OF SPECIMENS EXPOSED TO WET NTO
FOR 30 DAYS AT 70 C

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
	Ferrous Specimens		
304L	-0.0046	-0.181	Welded specimens showed greater weight loss than nonwelded specimens.
316	-0.0052	-0.229	None
321	-0.0054	-0.237	Vapor-phase specimen weight losses were slightly greater than liquid-phase specimens.
AM 350	-0.0077	-0.263	None
440	-0.0222	-0.962	Liquid-phase welded specimen showed a much smaller weight loss than others.
1018	-0.0017	-0.073	Vapor-phase specimens showed greater weight losses than liquid-phase specimens.
	Aluminum Specimens		
TENS-50	-0.0003	-0.037	Welded specimens showed greater weight loss than nonwelded specimens.
2014	-0.0004	-0.038	Vapor-phase welded specimen showed greater weight loss than others.
2024	-0.0005	-0.066	Vapor-phase specimen weight loss was 4 times that of liquid-phase specimen.
6061	-0.0002	-0.031	Liquid-phase nonwelded specimen showed weight increase.
7075	-0.0002	-0.018	Liquid-phase specimen showed no weight change.

TABLE A-7

WEIGHT CHANGES OF SPECIMENS EXPOSED TO DRY NTO + PNO_2
FOR 30 DAYS AT AMBIENT TEMPERATURE

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
Ferrous Specimens			
304 L	+0.0011	+0.046	The weight gain of the liquid-phase welded specimen was slightly less than the others.
316	+0.0005	+0.025	The liquid-phase weight gains were approximately 1.5 times those of the vapor phase.
321	+0.0006	+0.030	The vapor-phase nonwelded specimen exhibited approximately twice the weight gain of the other specimens.
AM 350	+0.0018	+0.061	The liquid-phase nonwelded specimen showed a smaller weight gain than other specimens.
440	+0.0021	+0.092	None
1018	+0.0020	+0.080	The welded specimens showed weight less than the nonwelded specimens.
Aluminum Specimens			
TENS-50	+0.0128	+1.726	None
2014	+0.0075	+1.068	Nonwelded specimens exhibited a slightly greater weight gain than welded specimens.
2024	+0.0056	+0.696	There was approximately the same weight gain for all specimens.
6061	+0.0243	+3.57	No weight was recorded for the liquid-phase welded sample; it was exposed to air and the passivation layer reacted.
7075	+0.0096	+0.892	None

TABLE A-8

WEIGHT CHANGES OF SPECIMENS EXPOSED TO DRY NTO + FNO_2
FOR 30 DAYS AT AMBIENT TEMPERATURE
(RERUN OF PREVIOUS TEST)

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
Aluminum Specimens			
TENS-50	+0.0130	+1.761	Liquid-phase specimens showed greater weight gains than vapor-phase specimens.
2014	+0.0072	+0.870	Liquid-phase specimens showed greater weight gains than vapor-phase specimens.
2024	+0.0098	+1.124	Liquid-phase specimen showed greater weight gain than vapor-phase specimen.
6061	+0.0088	+1.303	Liquid-phase specimens showed greater weight gains than vapor-phase specimens.
7075	+0.0075	+0.833	None

TABLE A-9

WEIGHT CHANGES OF SPECIMENS EXPOSED TO DRY NTO + FNO_2
FOR 30 DAYS AT 70 C

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
		Ferrous Specimens	
304L	+0.0006	+0.022	Liquid-phase nonwelded specimen showed a weight gain of about one-third of others.
316	-	-	Welded specimens showed small weight gains. Nonwelded specimens showed small weight losses.
321	+0.0003	+0.011	Liquid-phase welded specimen showed weight gain of at least twice those of others.
AM 350	+0.0026	+0.083	Welded specimens showed double the weight gain of nonwelded specimens.
440	+0.0280	+1.218	Nonwelded specimens showed larger weight gains than welded specimens.
1018	+0.0060	+0.260	Nonwelded specimens showed larger weight gains than welded specimens.
		Aluminum Specimens	
TENS-50	+0.0282	+3.59	None
2014	+0.0156	+1.670	None
2024	+0.0138	+1.720	Liquid-phase specimen showed weight gain 1.5 times that of vapor-phase specimen.
6061	+0.0234	+3.23	Liquid-phase welded specimen showed larger weight gain than others.
7075	+0.0203	+1.888	Liquid-phase specimen showed weight gain 1.5 times that of vapor-phase specimen.

TABLE A-10

WEIGHT CHANGES OF SPECIMENS EXPOSED TO WET NTO + FNO_2
FOR 30 DAYS AT AMBIENT TEMPERATURE

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
Ferrous Specimens			
304L	+0.0008	+0.038	Vapor-phase weight gains were approximately 2.5 times those of the liquid-phase.
316	+0.0004	+0.015	Liquid-phase weight gains were greater than those of the vapor-phase.
321	+0.0006	+0.030	Welded specimen weight gains were approximately half of the non-welded specimens.
AM 350	+0.0021	+0.072	Vapor-phase weight gains were greater than those of the liquid-phase.
440	+0.0027	+0.115	All weight changes were about equal.
1018	+0.0030	+0.146	Nonwelded specimens had greater weight gains than welded specimens.
Aluminum Specimens			
TENS-50	+0.0231	+2.36	All weight gains were about equal.
2014	+0.0114	+1.469	Liquid-phase weight gains were slightly greater than those of vapor-phase.
2024	+0.0063	+0.772	Liquid-phase specimen showed greater weight gain than vapor-phase specimen.
6061	+0.0368	+4.56	All weight changes were about equal.
7075	+0.0150	+1.399	Liquid-phase specimen showed greater weight gain than vapor-phase specimen.

TABLE A-11

WEIGHT CHANGES OF SPECIMENS EXPOSED TO WET NTO + FNO_2 FOR 30 DAYS AT 70 C

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
Ferrous Specimens			
304L	+0.0166	+0.678	Welded specimens showed smaller weight gains than nonwelded specimens.
316	+0.0088	+0.354	Welded specimens showed smaller weight gains than nonwelded specimens.
321	+0.0122	+0.582	Liquid-phase specimens showed weight gains about twice those of vapor-phase specimens.
AM 350	+0.0376	+1.284	Vapor-phase nonwelded specimen showed slightly greater weight gain than others.
440	+0.0408	+1.710	Welded specimens showed slightly smaller weight gains than nonwelded specimens.
1018	+0.0176	+0.652	Liquid-phase specimens showed greater weight gains than vapor-phase specimens.
Aluminum Specimens			
TENS-50	+0.1850	+23.17	Vapor-phase welded specimen showed much smaller weight gain than others.
2014	+0.0404	+5.39	Nonwelded specimens showed smaller weight gain than welded specimens.
2024	+0.0562	+6.84	Liquid-phase specimen weight gain was about twice that of the vapor-phase specimen.
6061	+0.1263	+18.87	Liquid-phase specimens showed weight gains about 4 times those of vapor-phase specimens.
7075	+0.1140	+10.67	Liquid-phase specimen showed weight gain about twice that of vapor-phase specimen.

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TABLE A-12

WEIGHT CHANGES OF SPECIMENS EXPOSED TO DRY NTO + HF
FOR 30 DAYS AT AMBIENT TEMPERATURE

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
Ferrous Specimens		
304 L	+0.0006	+0.029	Vapor-phase weight increases were greater than liquid-phase weight increases.
316	+0.0006	+0.025	Vapor-phase weight gains were twice those of liquid phase.
321	+0.0010	+0.044	Nonwelded specimens showed approximately twice the weight gain of welded specimens.
AM 350	+0.0023	+0.080	All specimens showed approximately the same weight increase. Welded specimens showed a slightly greater weight gain.
440	+0.0048	+0.216	All specimens showed approximately the same weight change.
1018	+0.0044	+0.191	The weight gain of the liquid-phase welded specimen was approximately one-third of the others.
Aluminum Specimens		
TENS-50	+0.0010	+0.125	All weight changes were approximately equal.
2014	+0.0009	+0.121	The vapor-phase welded specimen had a slightly greater weight gain than the others.
2024	+0.0004	+0.044	The liquid-phase specimen showed a significant weight gain. The vapor-phase specimen showed a slight weight.
6061	+0.0005	+0.070	Liquid-Phase specimens showed a slight weight change. Vapor-phase specimens showed a significant weight gain.
7075	+0.0012	+0.116	Both specimens showed approximately the same weight increase.

TABLE A-13

WEIGHT CHANGES OF SPECIMENS EXPOSED TO DRY NTO + HF
FOR 30 DAYS AT 70 C

Alloy	Average Weight Change, grams	Average Percent Weight Change	Comments
Ferrous Specimens		
304L	+0.0039	+0.157	Vapor-phase welded specimen showed larger weight gain than others.
316	+0.0050	+0.191	Vapor-phase specimens showed weight increases twice those of liquid-phase.
321	+0.0056	+0.244	None
AM 350	+0.0088	+0.294	Liquid-phase nonwelded specimen showed less of a weight gain than others.
440	+0.0447	+1.985	Welded specimens showed less of a weight gain than nonwelded specimens.
1018	+0.0362	+1.497	None
Aluminum Specimens		
TENS-50	+0.0282	+3.59	None
2014	+0.0131	+1.670	Liquid-phase specimens showed greater weight gains than vapor-phase specimens.
2024	+0.0138	+1.720	Liquid-phase specimen showed greater weight gain than vapor-phase specimen.
6061	+0.0234	+3.23	None
7075	+0.0102	+1.888	Liquid-phase specimen showed greater weight gain than vapor-phase specimen.

TABLE A-14

SURFACE CONDITION OF SPECIMENS EXPOSED TO DRY NTO
FOR 30 DAYS AT AMBIENT TEMPERATURE

Alloy	Phase	Comments
		Ferrous Specimens
304 L	Vapor	No effect
	Liquid	Crazing and very slight corrosion of machining grooves
316	Vapor	No effect
	Liquid	Very slight corrosion of machining grooves
321	Vapor	No effect
	Liquid	Very slight crazing and very slight corrosion of machining grooves
AM 350	Vapor	Slight surface attack
	Liquid	Very slight surface attack
440	Vapor	Pitting and apparent corrosion
	Liquid	Slight pitting and apparent machining groove corrosion
1018	Vapor	Bad pitting and scale formation
	Liquid	Bad pitting and scale formation
		Aluminum Specimens
TENS-50	Vapor	Very slight attack of machining grooves
	Liquid	Very slight attack of machining grooves
2014	Vapor	No effect
	Liquid	Very slight surface attack
2024	Vapor	No effect
	Liquid	No effect
6061	Vapor	No effect
	Liquid	Slight pitting and corrosion
7075	Vapor	No effect
	Liquid	No effect

TABLE A-15

SURFACE CONDITION OF SPECIMENS EXPOSED TO WET NTO
FOR 30 DAYS AT AMBIENT TEMPERATURE

Alloy	Phase	Comments
Ferrous Specimens		
304 L	Vapor	No effect
	Liquid	No effect
316	Vapor	No effect
	Liquid	No effect
321	Vapor	Very slight corrosion
	Liquid	Very slight corrosion and crazing
AM 350	Vapor	Very slight corrosion
	Liquid	Very slight corrosion
440	Vapor	Slight corrosion
	Liquid	Slight corrosion and spotting
1018	Vapor	Slight corrosion of machining grooves
	Liquid	Slight corrosion of machining grooves
Aluminum Specimens		
TENS-50	Vapor	Pitting and slight corrosion of weld surface
	Liquid	Slight pitting and surface corrosion
2014	Vapor	Slight corrosion
	Liquid	Very slight corrosion
2024	Vapor	Very slight corrosion on edge
	Liquid	Very slight corrosion
6061	Vapor	Slight corrosion and slight pitting
	Liquid	Very slight corrosion and slight pitting or spotting
7075	Vapor	Pitting and slight corrosion
	Liquid	Very slight pitting and slight corrosion

TABLE A-16

SURFACE CONDITION OF SPECIMENS EXPOSED TO DRY NTO
FOR 30 DAYS AT 70 C

Alloy	Phase	Comments
		Ferrous Specimens
304L	Vapor	Slight spotting and slight corrosion
	Liquid	No effect
316	Vapor	Slight pitting and spotting
	Liquid	Slight spotting and slight corrosion
321	Vapor	No effect
	Liquid	No effect
AM 350	Vapor	No effect
	Liquid	Very slight spotting and slight corrosion
440	Vapor	Apparent corrosion
	Liquid	Apparent corrosion
1018	Vapor	Bad corrosion
	Liquid	Bad corrosion
		Aluminum Specimens
TENS-50	Vapor	Very slight corrosion and very slight spotting
	Liquid	Very slight corrosion and slight spotting
2014	Vapor	No effect
	Liquid	Very slight corrosion and very slight spotting
2024	Vapor	No effect
	Liquid	Very slight corrosion and slight spotting
6061	Vapor	No effect
	Liquid	No effect
7075	Vapor	No effect
	Liquid	No effect

TABLE A-17

SURFACE CONDITION OF SPECIMENS EXPOSED TO WET NTO
FOR 30 DAYS AT 70 C

Alloy	Phase	Comments
		Ferrous Specimens
204L	Vapor	Slight spotting and corrosion
	Liquid	Slight spotting
316	Vapor	Spotting
	Liquid	Slight discoloring and slight corrosion
321	Vapor	Very slight corrosion and slight discoloring
	Liquid	Very slight corrosion and slight spotting
AM 350	Vapor	Very slight corrosion and slight discoloring
	Liquid	No effect
440	Vapor	Slight corrosion and discoloring
	Liquid	Slight corrosion and discoloring
1018	Vapor	Corrosion and flaking surface layer
	Liquid	Corrosion and flaking surface layer
		Aluminum Specimens
TENS-50	Vapor	No effect
	Liquid	No effect
2014	Vapor	No effect
	Liquid	No effect
2024	Vapor	Some dark spots
	Liquid	No effect
6061	Vapor	No effect
	Liquid	Slight spotting and slight corrosion
7075	Vapor	No effect
	Liquid	No effect

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TABLE A-18

SURFACE CONDITION OF SPECIMENS EXPOSED TO DRY NTO + FNO_2 FOR 30 DAYS AT AMBIENT TEMPERATURE

Alloy	Phase	Comments
		Ferrous Specimens
304L	Vapor	Slight surface layer
	Liquid	Very slight surface layer
316	Vapor	No effect
	Liquid	Slight surface layer and spotting
321	Vapor	Slight surface layer and spotting
	Liquid	No effect
AM 350	Vapor	Very slight surface layer
	Liquid	Slight surface layer and spotting
440	Vapor	Surface layer and spotting
	Liquid	Apparent surface layer
1018	Vapor	Surface layer and spotting
	Liquid	Surface layer and spotting, apparent residue on welded sample
		Aluminum Specimens (Rerun of initial test)
TENS-50	Vapor	Apparent passivation layer
	Liquid	Apparent passivation layer
2014	Vapor	Thin, spotted passivation layer
	Liquid	Thin, spotted passivation layer
2024	Vapor	Thin passivation layer
	Liquid	Thin passivation layer
6061	Vapor	Passivation layer
	Liquid	Thin passivation layer
7075	Vapor	Passivation layer
	Liquid	Thin passivation layer

TABLE A-19

SURFACE CONDITION OF SPECIMENS EXPOSED TO DRY AND WET
NTO + NO_2 FOR 30 DAYS AT 70 C

Alloy	Phase	Comments
Ferrous Specimens, Dry		
340L	Vapor	Extremely thin surface layer
	Liquid	Extremely thin surface layer
316	Vapor	Extremely thin surface layer
	Liquid	Extremely thin surface layer
321	Vapor	Very thin surface layer
	Liquid	Very thin, spotty surface layer
AM 350	Vapor	Very thin surface layer
	Liquid	Very thin surface layer
440	Vapor	Heavy, loose surface layer
	Liquid	Spotted surface layer
1018	Vapor	Spotted surface layer
	Liquid	Spotted surface layer
Ferrous Specimens, Wet		
304L	Vapor	Heavy, irregular surface layer
	Liquid	Heavy, irregular surface layer
316	Vapor	Heavy, spotted surface layer
	Liquid	Crazed surface layer
321	Vapor	Heavy surface layer
	Liquid	Heavy, crazed surface layer

Alloy	Phase	Comments
Ferrous Specimens, Wet		
AM 350	Vapor	Spotted surface layer
	Liquid	Heavy surface layer
440	Vapor	Heavy, light colored surface layer
	Liquid	Heavy, spotted surface layer
1018	Vapor	Spotted surface layer
	Liquid	Heavy spotted surface layer

The passivation layers on the aluminum specimens for both of the above tests reacted and disappeared before photomicrographs could be taken. Photographs of these specimens can be seen in Fig.   and

TABLE A-20

SURFACE CONDITION OF SPECIMENS EXPOSED TO WET NTO + FNO_2
FOR 30 Da ʹᵀ AMBIENT TEMPERATURE

Alloy	Phase	Comments
		Ferrous Specimens
304L	Vapor	Slight discoloring and surface layer
	Liquid	Slight discoloring and surface layer
316	Vapor	Slight discoloring and spotty surface layer
	Liquid	Very slight discoloring and thin surface layer
321	Vapor	Slight discoloring and spotty surface layer
	Liquid	Slight discoloring and spotty surface layer
AM 350	Vapor	Slight surface layer and discoloring
	Liquid	Slight surface layer and discoloring
440	Vapor	Apparent dark spotted surface layer
	Liquid	Apparent spotted surface layer
1018	Vapor	Apparent spotted surface layer
	Liquid	Apparent spotted surface layer
		Aluminum Specimens
TENS-50	Vapor	Loose passivation layer
	Liquid	Loose passivation layer
2014	Vapor	Apparent passivation layer
	Liquid	Apparent passivation layer
2024	Vapor	Thin passivation layer
	Liquid	Thin passivation layer
6061	Vapor	Loose passivation layer and crazed surface
	Liquid	Crazed passivation layer
7075	Vapor	Apparent passivation layer
	Liquid	Crazed passivation layer

TABLE A-21

SURFACE CONDITION OF SPECIMENS EXPOSED TO DRY NTO + HF
FOR 30 DAYS AT AMBIENT TEMPERATURE

Alloy	Phase	Comments
		Ferrous Specimens
304 L	Vapor	Slight surface layer
	Liquid	Spotted surface layer
316	Vapor	No effect
	Liquid	Spotting on slight surface layer
321	Vapor	Slight surface layer
	Liquid	Spotting on slight surface layer
AM 350	Vapor	Very slight spotting on slight surface layer
	Liquid	Very slight spotting on surface layer
440	Vapor	Spotted surface layer
	Liquid	Spotted surface layer; dense layer on nonwelded specimen
1018	Vapor	Apparent spotting on surface layer
	Liquid	Spotted surface layer
		Aluminum Specimens
TENS-50	Vapor	Spotted passivation layer
	Liquid	Spotted passivation layer
2014	Vapor	No effect
	Liquid	No effect
2024	Vapor	No effect
	Liquid	No effect
6061	Vapor	Apparent surface crazing
	Liquid	Slight passivation layer
7075	Vapor	Slight passivation layer
	Liquid	Passivation layer

TABLE A-22

SURFACE CONDITION OF SPECIMENS EXPOSED TO DRY NTO + HF
FOR 30 DAYS AT 70 C

Alloy	Phase	Comments
		Ferrous Specimens
304L	Vapor	Spotted, very thin surface layer
	Liquid	Spotted, very thin surface layer
316	Vapor	Spotted, thin surface layer
	Liquid	Spotted, thin surface layer
321	Vapor	Slight spotting and very thin surface layer
	Liquid	Spotted, very thin surface layer
AM 350	Vapor	Very thin, spotty surface layer
	Liquid	No effect
440	Vapor	Extremely heavy flaking surface layer
	Liquid	Extremely heavy flaking surface layer
1018	Vapor	Heavy, spotted, light colored surface layer
	Liquid	Spotted, light colored slaking surface layer
		Aluminum Specimens
TENS-50	Vapor	Very thin passivation layer
	Liquid	Very thin passivation layer
2014	Vapor	Thin passivation layer
	Liquid	Passivation layer
2024	Vapor	Very thin passivation layer
	Liquid	Passivation layer
6061	Vapor	Passivation layer
	Liquid	Passivation layer
7075	Vapor	Passivation layer
	Liquid	Passivation layer

APPENDIX B

DATA ON EFFECTS OF FLOWING INTO UPON VALVES

TABLE B-1

ANALYSIS OF INHIBITED NITROGEN TETROXIDE
USED FOR THE SED PROPELLANT VALVE

Propellant	Original Water Content	Weight Percent FNO_2 Before Test	FNO_2 After Test
Dry NTO	0.08	5	5
Wet NTO	0.18	5	5

PROPELLANT VALVES PRE- AND POST-FUNCTIONAL TESTS

Valve No./Size	INTO Composition	Pre-Test Functional					
		300 psi					
		Pull-in Time at 26 Volts, second	Drop-out Time at 26 Volts, second	Pull-in Current at 26 Volts, ampere	Drop-out Current at 26 Volts, ampere	Leakage, cc/min	Pu at 2 s
1/25 lb ⎫	Mil-Spec with	0.0031	0.0011	0.13	0.032	0	0
2/100 lb ⎭	Inhibitor	0.0166	0.0027	0.27	0.052	0	0
3/100 lb ⎫	Wet NTO with	0.0158	0.0023	0.26	0.055	0	0
4/25 lb ⎭	Inhibitor	0.0042	0.0012	0.17	0.030	0	0
						Post-Test Functional	
1/25 lb ⎫	Mil-Spec with	0.0034	0.0012	0.138	0.032	<1	0
2/100 lb ⎭	Inhibitor	0.0165	0.0024	0.29	0.055	0	0
3/100 lb ⎫	Wet NTO with	0.016	0.0030	0.225	0.060	<1	0
4/25 lb ⎭	Inhibitor	0.0044	0.0014	0.195	0.032	0	0

VALVES PRE- AND POST-FUNCTIONAL TESTS

Pre-Test Functional			0 psi			
Pull-in ... at 26 Volts, ampere	Drop-out Current at 26 Volts, ampere	Leakage, cc/min	Pull-in Time at 26 Volts, second	Drop-out Time at 26 Volts, second	Pull-in Current at 26 Volts, ampere	Drop-out Current at 26 Volts, ampere
	0.032	0	0.0028	0.0014	0.095	0.022
	0.052	0	0.0087	0.0035	0.136	0.032
	0.055	0	0.0083	0.0031	0.135	0.036
	0.030	0	0.0027	0.0013	0.10	0.030
Post-Test Functional						
8	0.032	<1	0.0028	0.0014	0.095	0.025
	0.055	0	0.0094	0.0040	0.135	0.035
5	0.060	<1	0.0082	0.0030	0.125	0.040
5	0.032	0	0.0030	0.0015	0.105	0.025

TABLE B-3

DETAILED VALVE DISASSEMBLY INSPECTION DATA*

NO. 1, 25-POUND-THRUST VALVE

Seat

White crystalline material downstream of seat (fairly heavy deposit);
seat was clean (Fig. B-7).

Armature/Ball

Etched except for one circular spot evidently where seated (Fig. B-8).
Film in evidence on armature and deposited in holes (Fig. B-9).
Film-coating on armature, very fine etch (Fig. B-10).

Bore

Pole face etched with slight deposit (Fig. B-11).

NO. 2, 100-POUND-THRUST VALVE

Seat

Comparatively clean; a few flakes of crystalline material; clean down-
stream; immediately upstream speckled with green crystalline deposit
(Fig. B-12).

Armature/Ball

Seat area bright and shiny, finish unaffected, other part of ball etched;
few crystals of white-green material on seated portion of ball (Fig. B-13).
Heavy buildup of deposit on wall, and armature would not drop out of
housing freely; the armature had to be pushed from the filter side to
remove from housing (Fig. B-14).

Bore

Heavy buildup of material on walls especially in area at upper portion
of armature wall (Fig. B-16); pole face has quite a bit of buildup also
(Fig. B-15).

---

*Although a buildup of material was visibly apparent on all surfaces exposed
to the propellant, no deterrent effect on valve performance resulted (Table B-2).

TABLE B-3

(Concluded)

NO. 3, 100-POUND-THRUST VALVE

Seat

Clean with some crystalline material upstream very uniformly deposited (Fig. B-17).

Armature/Ball

Two places indicating seating; one bright and hardly etched, the other etched but not as much as the previous valve (Fig. B-18). Crystalline deposits all around bell area and holes, possibly not as much as in valve No. 2. Wall of armature has film uniformly deposited (Fig. B-19). Deposit not heavy, armature was easily removed from valve.

Bore

Wall had heavy deposit at point where wall and armature meets bore wall for about 1/8 to 1/4 inch down. Area above very clean, not deposited (Fig. B-20). Uniform light deposit or film over area of pole face (Fig. B-4).

NO. 4, 25-POUND-THRUST VALVE

Seat

Heavy deposit upstream and on upper portion of seat. Seat had quite a bit of salts deposited on downstream side (Fig. B-22).

Armature Ball

Etched slightly except for area where ball seated, some salts around ball (Fig. B-23). Light film covering armature and speckled raised deposit on walls, holes, and around ball (Fig. B-24).

Bore

Pole face had only slight film of deposit (Fig. B-25).

IHD61-9/17/64-C1R

Figure B-1. 25-Pound-Thrust Propellant Valve

1HD61-9/17/64-C1C

Figure B-2.   100-Pound-Thrust Propellant Valve

BORE ID
$0.2816^{+0.0008}_{-0.0004}$

ARMATURE OD
$0.2793^{+0.0000}_{-0.0004}$

STROKE
$0.0100^{+0.0015}_{-0.0022}$

FINISH

BORE 8⌄

ARMATURE 8⌄

347 SS

347 SS

430F SS

321 SS

430F SS

HAYNES STELLITE NO. 3

TEFLON

17-7 PH SS

430F SS

Figure B-3.   25-Pound-Thrust Propellant Valve

B-9
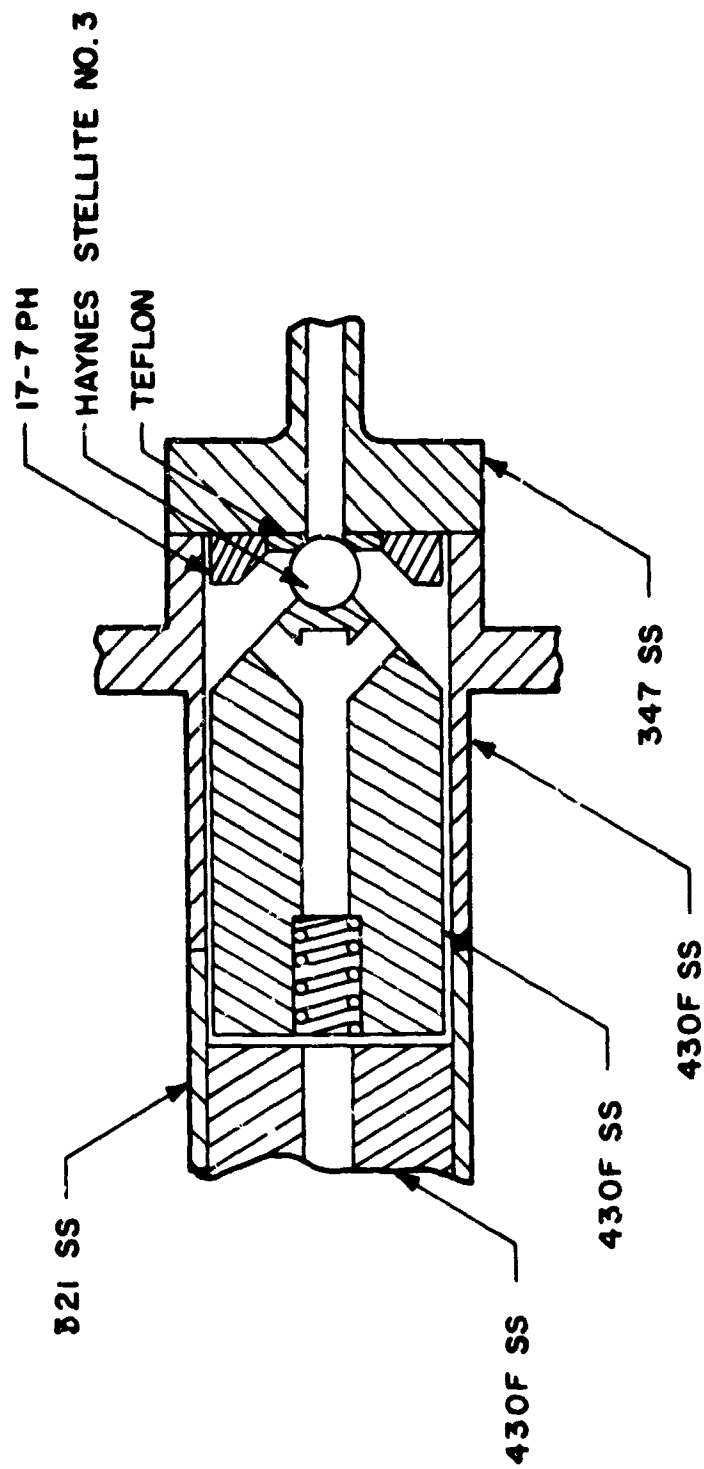
Figure B-4. 100-Pound-Thrust Propellant Valve
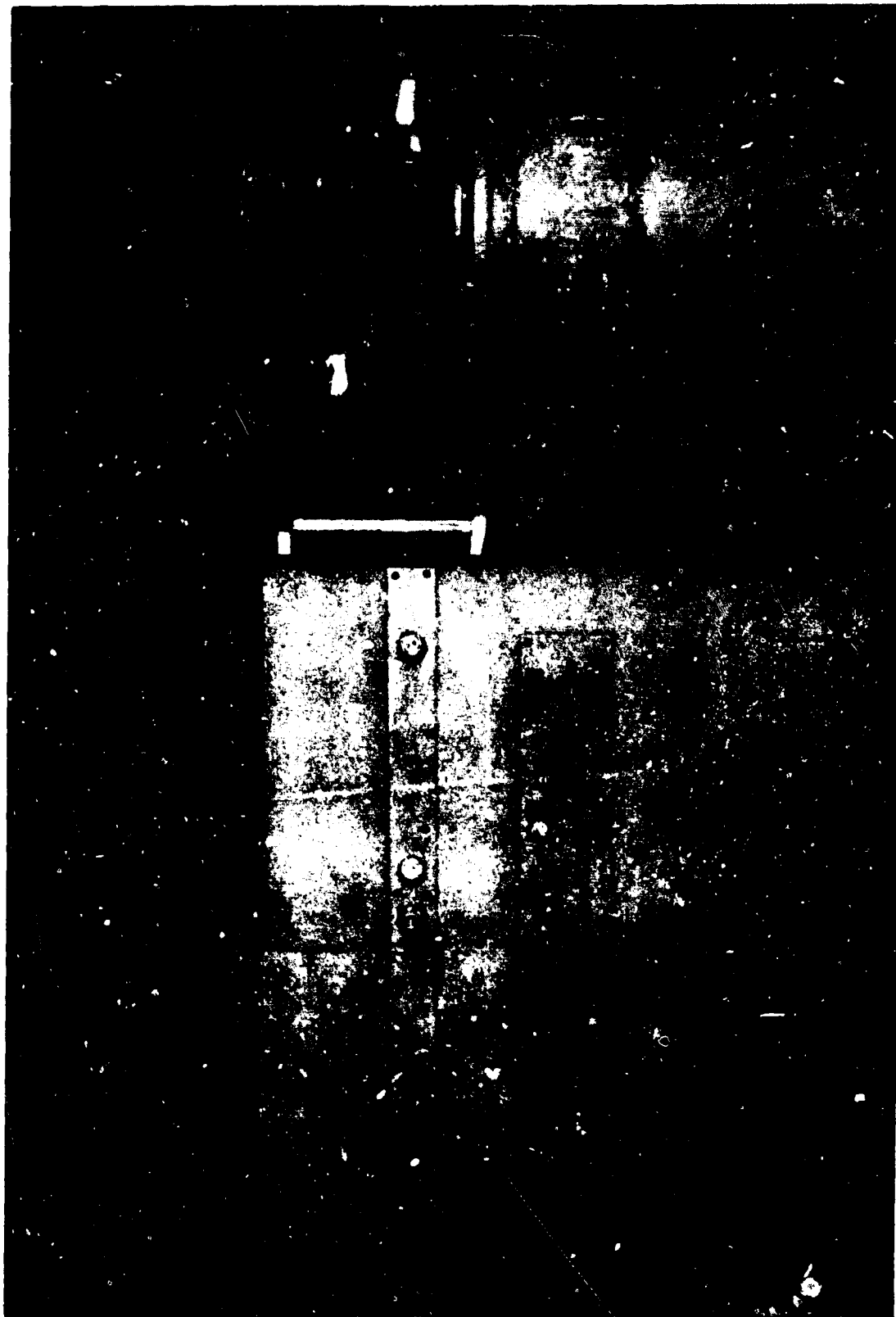
Figure B-5. Test Apparatus

5AA86-8/29/66-CLA

Figure B-6.   Interior of Test Apparatus

1EC65-9/26/66-C1A

Figure B-7. 25-Pound-Thrust Valve No. 1, View 1
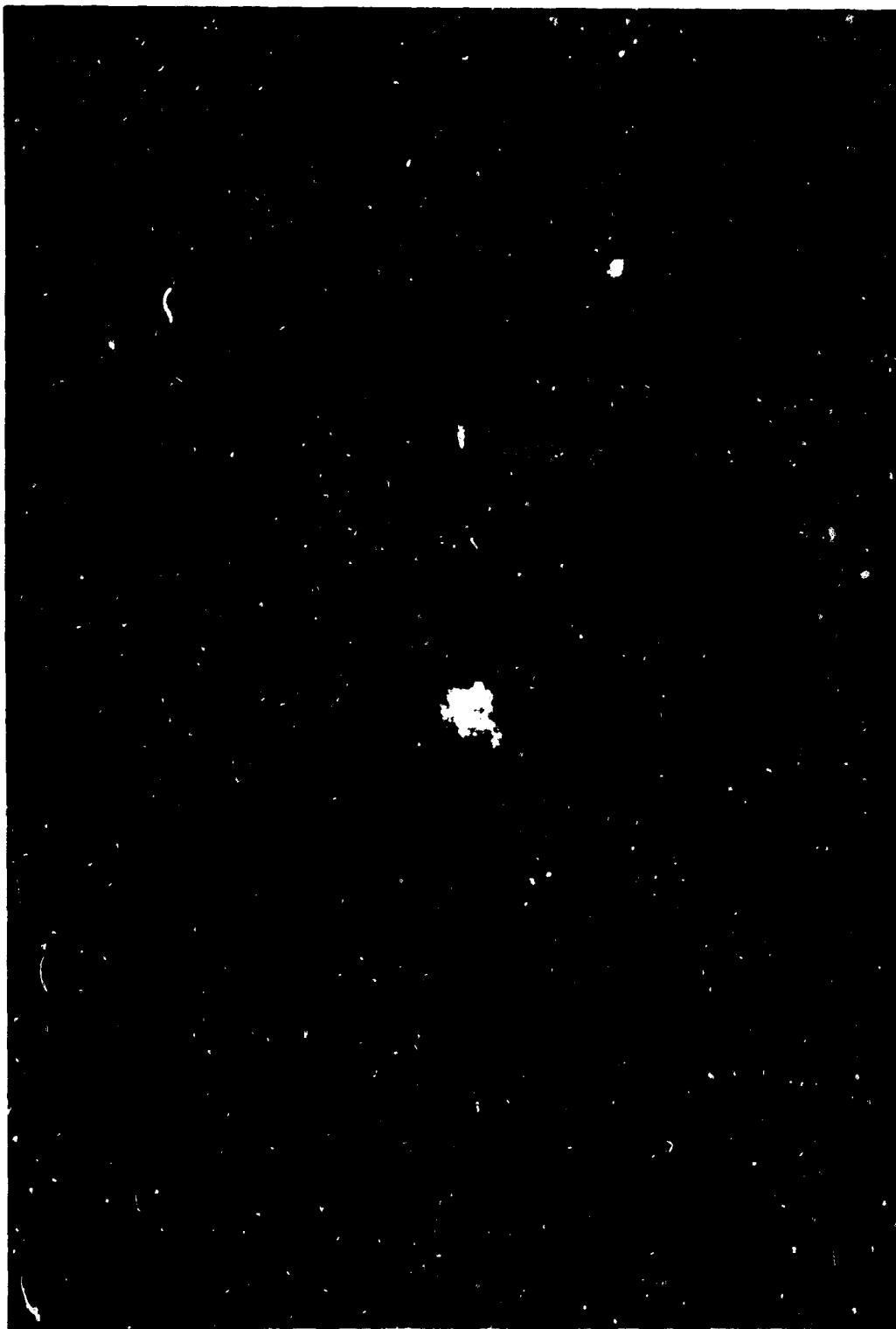
1EC65-9/26/66-C1D

Figure B-8.   25-Pound Thrust Valve No. 1, View 2

B-14

1BC65-9/26/66-C1B

Figure B-9.   25-Pound-Thrust Valve No. 1, View 3

B-15

1EC65-.. .6/66-C1C

Figure B-10. 25-Pound-Thrust Valve No. 1, View 4

1EC65-9/26/66-C1E

Figure B-11. 25-Pound-Thrust Valve No. 1, View 5

1BC65-9/26/66-C1K

Figure B-12.   100-Pound-Thrust Valve No. 2, View 1

1E65-9/26/66-C1N

Figure B-15. 100-Pound-Thrust Valve No. 2, View 2

1EC65-9/26/66-CIM
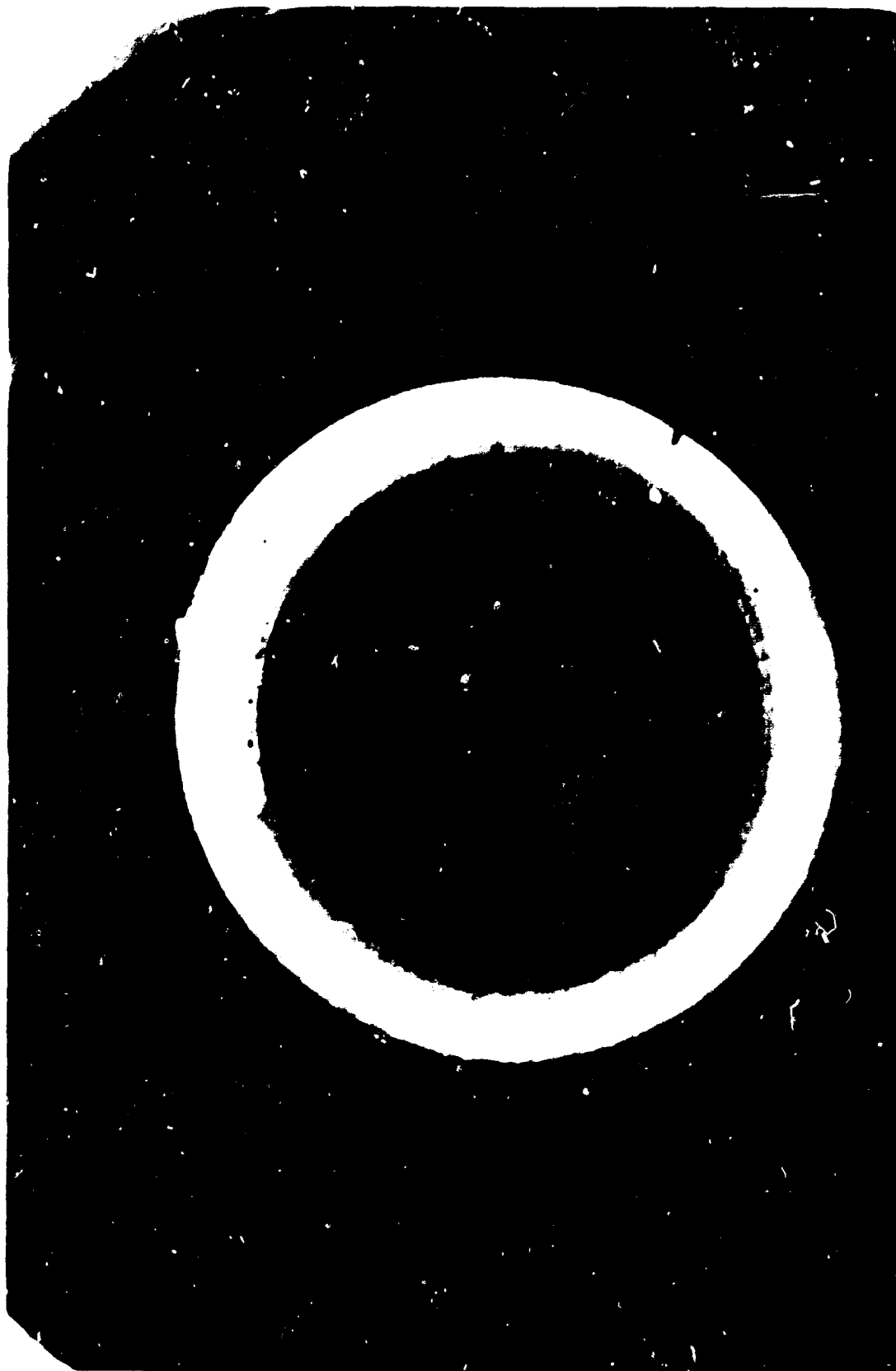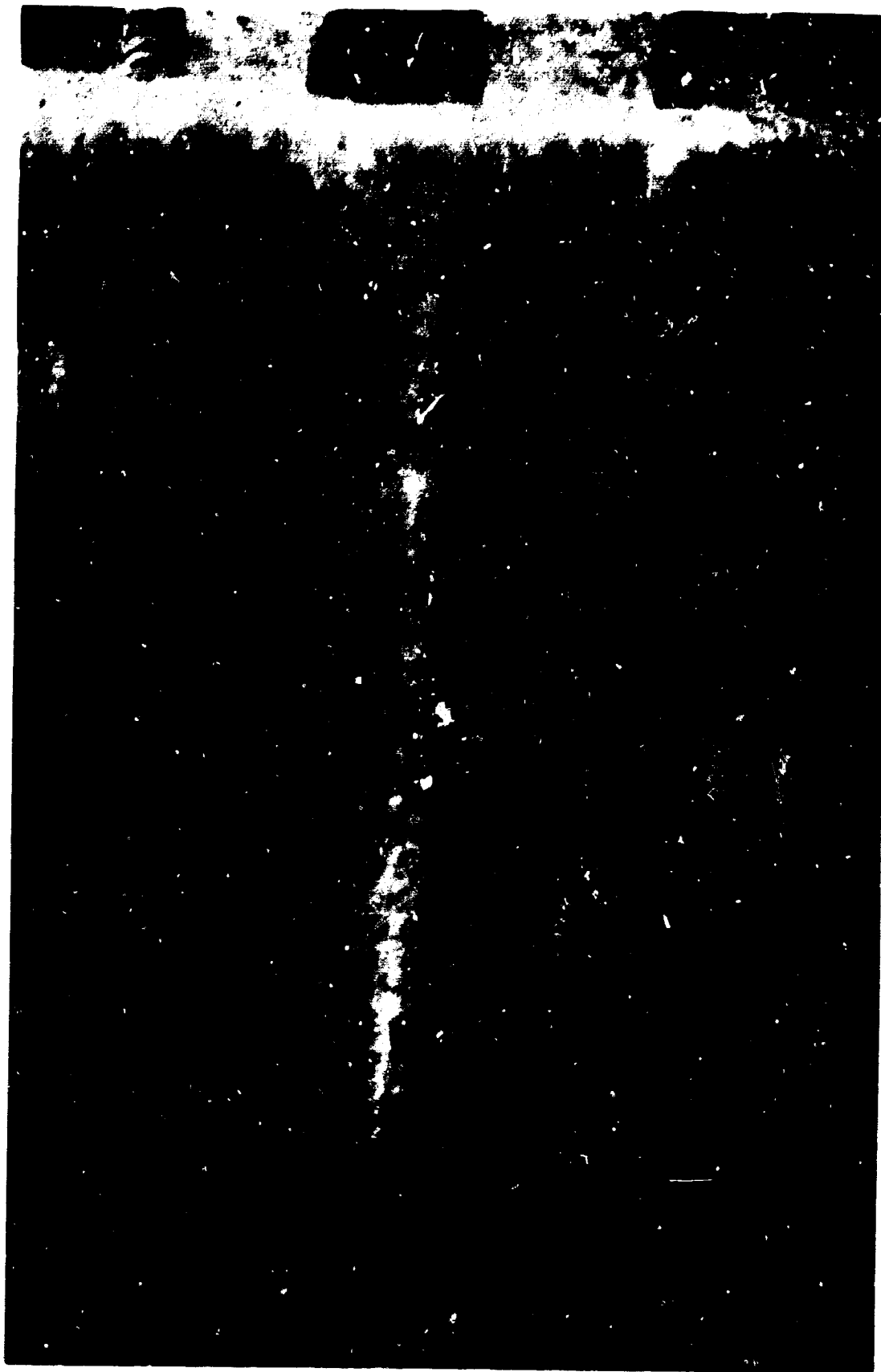
Figure B-14. 100-Pound-Thrust Valve No. 2, View 3

Figure B-15. 100-Pound-Thrust Valve No. 2, View 4
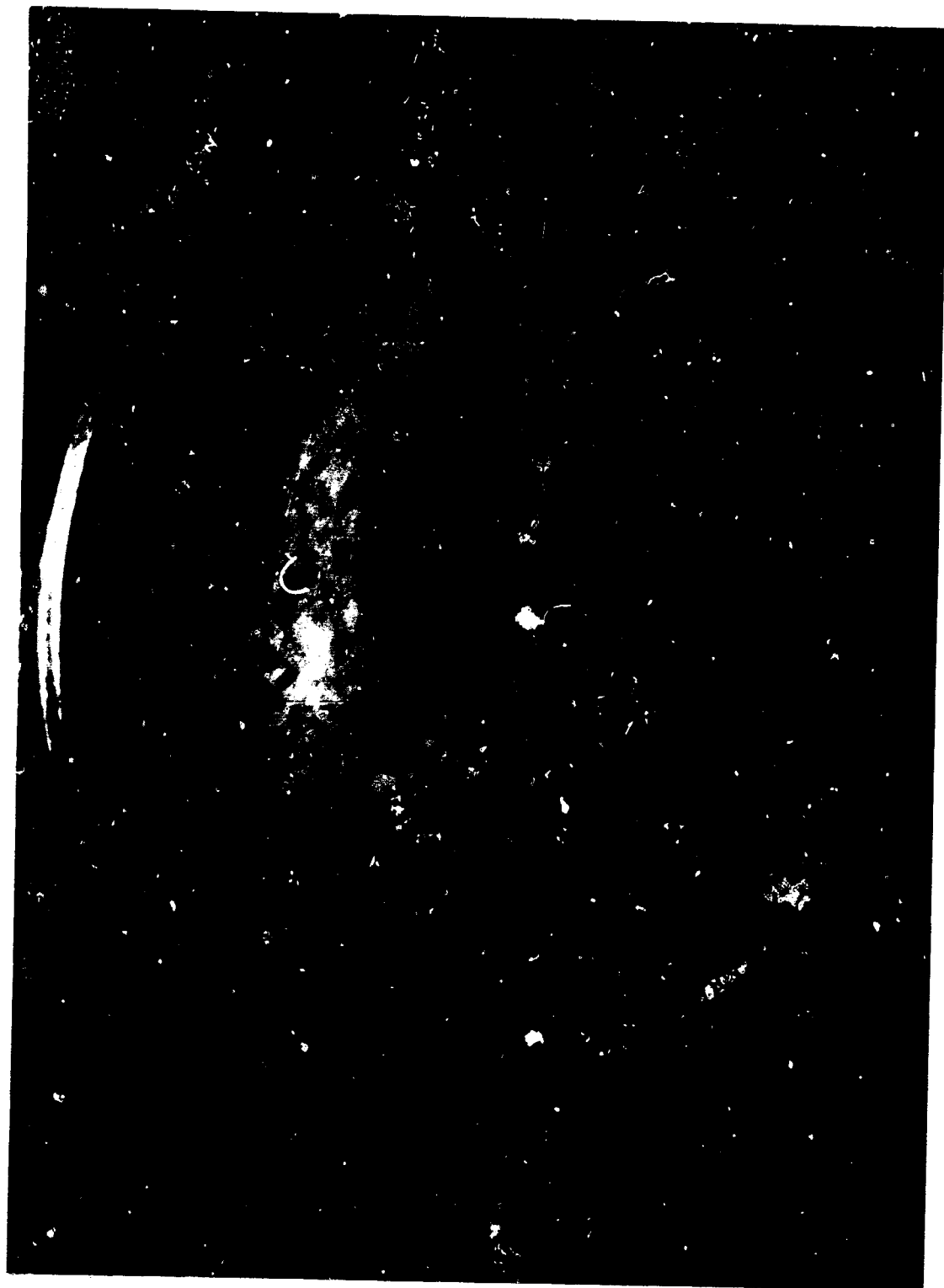
1E65-9/26/66-C1J

1EC65-9/26/66-C1L

Figure B-16. 100-Pound-Thrust Valve No. 2, View 5
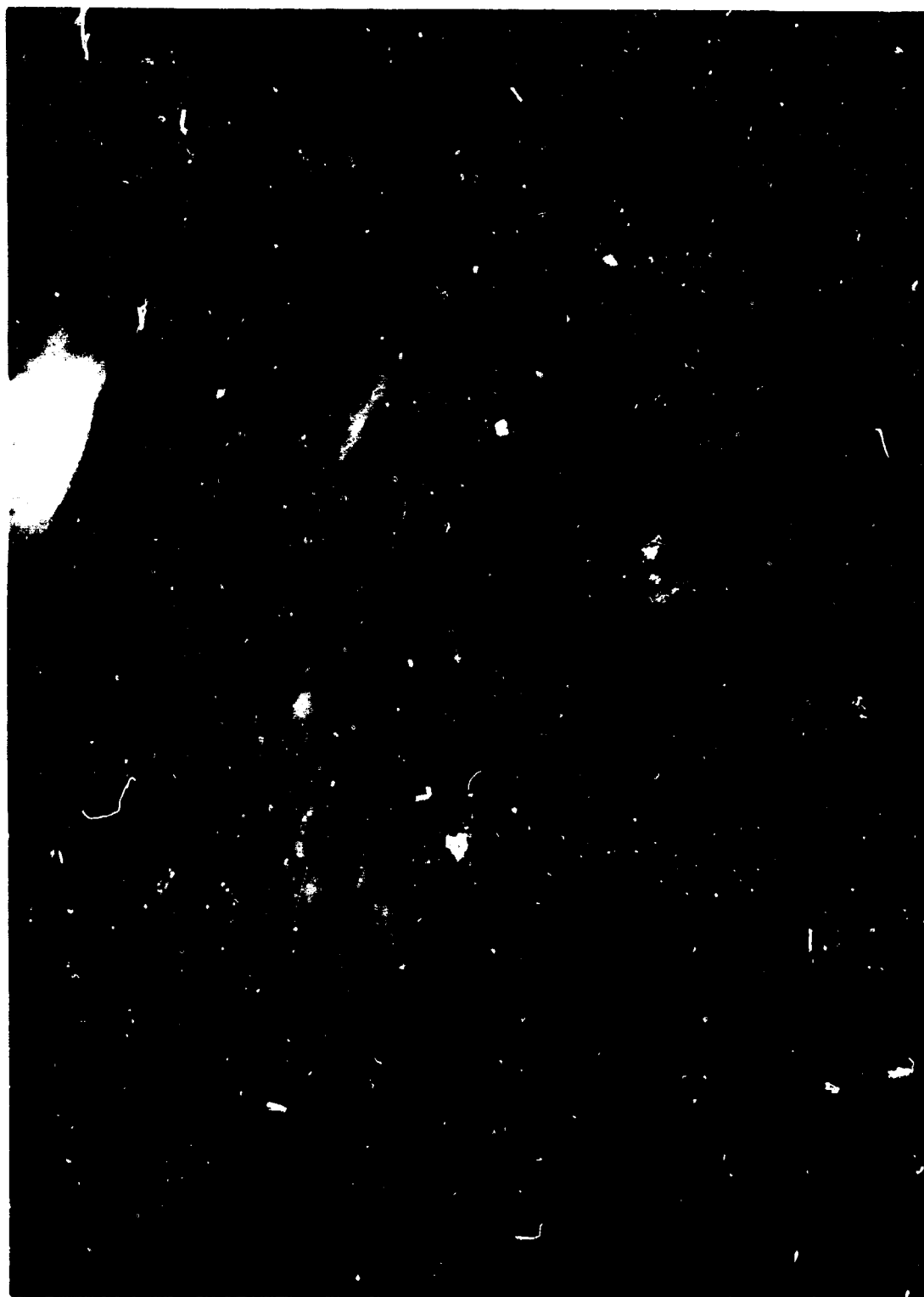
Figure B-17. 100-Pound-Thrust Valve No. 3, View 1

1BC65-9/26/66-C10

1E65-9/26/66-CLP

Figure B-18. 100-Pound-Thrust Valve No. 3, View 2

Figure B-19. 100-Pound-Thrust Valve No. 3, View 3

1EC65-9/26/66-C1Q

1EC65-9/26/66-CLR

Figure B-20. 100-Pound-Thrust Valve No. 3, View 4

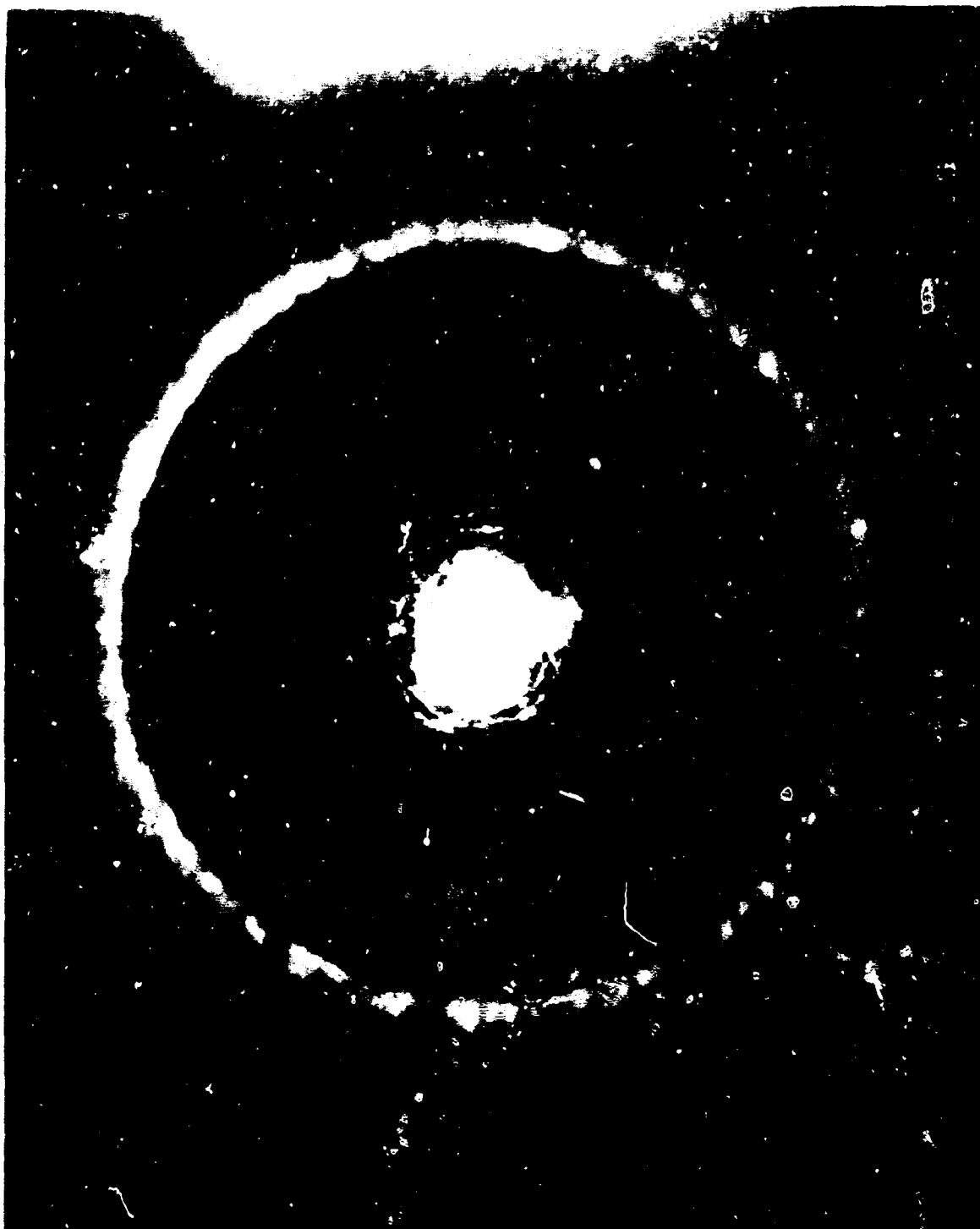Figure B-21. 100-Pound-Thrust Valve No. 3, View 5

1EC65-9/26/66-C1S

1HC65-9/26/66-C1H

Figure B-22. 25-Pound-Thrust Valve No. 4, View 1

LRC65-9/26/6c-C11

Figure B-23. 25-Pound-Thrust Valve No. 4, View 2

1EC65-9/26/66-C1F

Figure B-24. 25-Pound-Thrust Valve No. 4, View 3

1EC65-9/26/66-C1G

Figure B-25. 25-Pound-Thrust Valve No. 4, View 4

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10. AVAILABILITY/LIMITATION NOTICES

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Air Force Rocket Propulsion Laboratory Research and Technology Division Edwards, California

13. ABSTRACT This program is concerned with evaluating a new storable liquid oxidizer INTO, which is nitrogen tetroxide (NTO) inhibited with a fluorine oxidizer. The best fluorine oxidizer has been found to be FNO_2. Storability tests of INTO in stainless-steel, aluminum, and nickel containers at 70 C have now been in progress for 6 months with no apparent change in the composition of the propellants. Corrosion tests of steel and aluminum alloys are being conducted in wet NTO, dry NTO, INTO made from wet NTO, INTO made from dry NTO, and dry NTO + HF. The tests are being conducted at ambient temperature for 30 days and for 20 months, and at 70 C for 30 days. The results of the 30-day tests are reported herein. A definite passivation layer was noted both visually and by weight change on the aluminum samples exposed to INTO at both temperatures and on the iron samples exposed to INTO and to NTO + HF at 70 C. INTO made from wet and dry NTO has been intermittently flowed through 25- and 100-pound valves for a 2 week period with no apparent deterent effects upon valve performance. INTO has been prepared by bubbling F_2 through liquid-propellant-grade NTO at ambient temperature. The reaction proceeded smoothly and no difficulties are anticipated in scaling up the operation. The conductivities of INTO and NTO solutions have been measured. The addition of FNO_2 or F_3NO to NTO caused only a small change in conductivity. It is not anticipated that INTO will present more galvanic corrosion problems then does NTO. Measurements of the vapor pressures and freezing points of INTO solutions have been completed. Methods have been developed for the chemical analysis of INTO and of NTO.

DD FORM 1473 JAN 64

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Liquid Oxidizers						
Nitrogen Tetroxide						
Fluorine						
Corrosion						
Storability						
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